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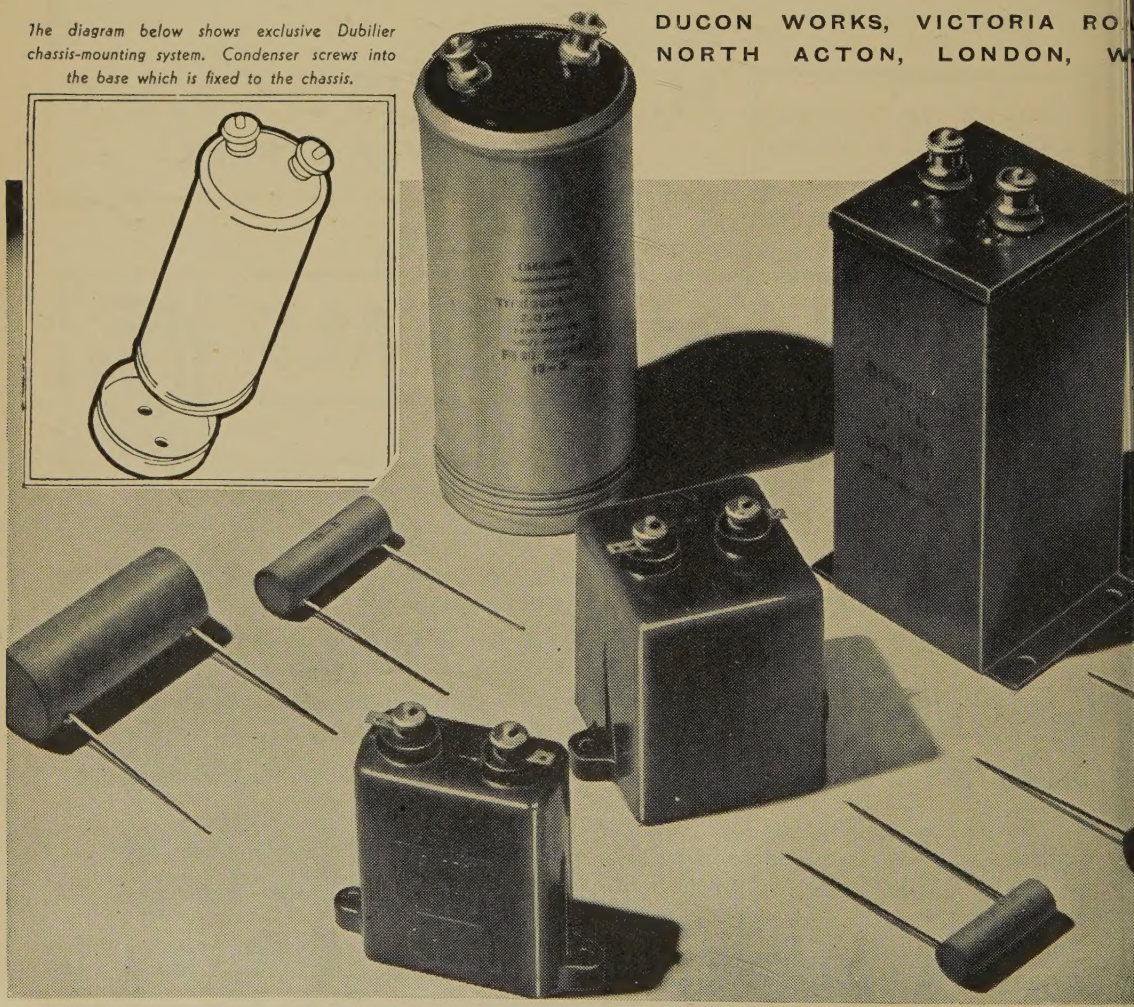

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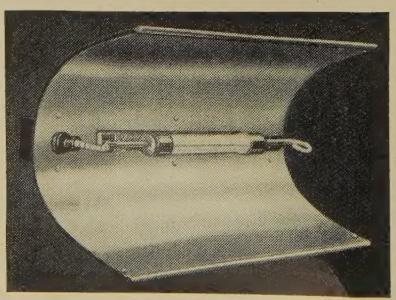

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INTENSITIES IN THE PRINCIPAL SERIES OF LITHIUM

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ABSTRACT. The effect of using orthogonal instead of non-orthogonal wave functions in the calculation of the oscillator-strengths (f numbers) of the first three lines of the principal series of lithium has been investigated. The Hartree self-consistent field method is employed to calculate the ($1s$) radial wave function, and the ($2s$) radial wave function is made orthogonal to the ($1s$) by linear combination. The orthogonal functions have been used to calculate the energies of the optical terms ($2s$), ($2p$), ($3p$) and ($4p$), and the f numbers of the first three lines of the principal series. Very satisfactory agreement with observed values is obtained for the energies (the maximum difference being 3 per cent). The agreement for the f numbers is not so good, but is better than when non-orthogonal functions are used.

§ 1. INTRODUCTION

QUANTUM theory considers emission of radiation by atoms or molecules to take place as the result of a transition from a state of higher to a state of lower energy. The emitted intensity I of the spectral line corresponding to the transition from the state r to the state s is given in ergs per second by

I

r, s

$$I = N_r A_{rs} h\nu_{rs},$$

where N_r is the number of atoms in the state r and A_{rs} is the Einstein[1] spontaneous-emission probability.

N_r, A_{rs}

It is convenient to introduce a set of quantities called *oscillator-strengths* or *f numbers*† in terms of which the intensity is given by

f

$$I = N_r (g_s/g_r) . (8\pi^2 e^2 h/mc^3) . \nu_{rs}^3 . f_{rs},$$

i.e. the intensity is proportional to the cube of the frequency ν_{rs}, and to the f number.

ν_{rs}

The first wave-mechanical calculations of the transition probabilities were made by Schrödinger, Sugiura, and Kupper[2]. Dirac[3] has shown that the coefficients A_{rs} may be expressed in terms of the matrix amplitudes for the transition r to s. These will be considered in more detail in § 6.

Before the oscillator-strength of a line in the series spectrum of an atom can be estimated it is necessary to obtain the wave functions and the energies of the

† For a fuller discussion of the oscillator-strengths, see Condon and Shortley's *Theory of Atomic Spectra*, Chapter IV (Camb. Univ. Press, 1936).

normal and excited states of the atom. For hydrogen this presents no difficulty as, on account of the inverse-square-law character of the field, the wave equations can be solved exactly. However, for the many-electron atoms an exact solution of the problem of the determination of the wave function is not known, but approximations to it have been made by Hartree[4], Slater[5], and Fock[6].

Hargreaves[7] used Hartree's method for the numerical solution of the Schrödinger wave equation for an atom with a non-Coulomb field of force, to estimate the oscillator strengths of the lines in the principal series of lithium. Hartree's method does not take into account either the effects of interchange of electrons between the one-electron wave functions, or Pauli's principle. Slater[5] has shown how, by using a more accurate form of the wave function, it is possible to take into account the effects of interchange, and to calculate the energies of the optical terms from the parameters of the central-field problem and corresponding one-electron wave functions. McDougall[8], basing his work on Slater's, has calculated the optical terms of Si^{+3}; the stationary states there calculated are essentially states of a series electron outside a core consisting of closed shells; the perturbation of the core by the series electron is then small and can be neglected, so that the states of Si^{+3} can be taken as a Si^{+4} structure with an additional wave function for the series electron.

We shall adopt here a similar simplification, namely that the states of lithium may be taken as a Li^{+} structure with an additional wave function for the series electron. Slater's results, in so far as they are required for this paper, are briefly restated in §§ 2 and 3.

The object of this paper is to compare the oscillator strengths f, using different approximations to the one-electron wave functions. The ($2s$) wave function used by Hargreaves was not orthogonal to the other one-electron wave functions. The author has calculated the ($1s$) wave function, and the ($2s$) wave function is made orthogonal to the ($1s$). Next, the energies of the normal and excited states are calculated by Slater's and McDougall's methods, by means of these orthogonal wave functions. Finally, the oscillator-strengths for the ($2s$–$2p$), ($2s$–$3p$), and ($2s$–$4p$) transitions calculated from (*a*) non-orthogonal wave functions of Hargreaves, (*b*) orthogonal wave functions of the author, and (*c*) Fock wave functions, are compared with one another.

§ 2. GENERAL THEORY

Ψ The wave function Ψ of the stationary states of an atomic system consisting of
n n electrons are given by making $\int \Psi H \Psi^* d\tau$ stationary for a normalized Ψ,† where
H H is the Hamiltonian operator defined by the equation

$$H = \sum_{j=1}^{n} [-\tfrac{1}{2}\nabla_j^2 - N/r_j] + \sum_{j=1}^{n} \sum_{k=j+1}^{n} 1/r_{jk} \qquad \text{.....(1),}$$

N for an atom of atomic number N.‡ We have neglected the spin and relativity contributions to the Hamiltonian.

† Cf. Condon and Shortley, *Theory of Atomic Spectra*, Chapter VI.
‡ Atomic units are used throughout. For these, see Hartree[4].

Let us denote the individual electron wave functions by $\psi(\alpha/1), \psi(\beta/2), \ldots, \psi(\omega/n)$ where the Greek letters $\alpha, \beta, \gamma, \ldots, \omega$ refer to the wave functions and the numbers 1, 2, 3, ..., n to the coordinates (including spin) of the electrons. ψ $\alpha \ldots \omega$ 1 ... n

A general form of Ψ which conforms with Pauli's principle is the antisymmetric form, written as a determinant, thus

$$\Psi = \frac{1}{\sqrt{(n!)}} \begin{vmatrix} \psi(\alpha/1) & \psi(\beta/1) \ldots \psi(\omega/1) \\ \psi(\alpha/2) & \\ \vdots & \\ \psi(\alpha/n) & \psi(\omega/n) \end{vmatrix} \qquad \ldots\ldots(2).$$

It is usually assumed that the one-electron wave functions are solutions of Schrödinger's equation for an electron in a central field, thus

$$\psi(\alpha/j) = \frac{1}{r} P(n_\alpha l_\alpha / r_j)\, S(l_\alpha m_\alpha / \theta_j \phi_j)\, \chi(s_\alpha / s_j) \qquad \ldots\ldots(3),$$

in the usual notation; P is a function of r only, S is the spherical harmonic of degree l_α, and χ is the spin wave function. P, S l_α, χ

The analytical work of evaluating the integrals for the energies and the oscillator-strengths, with wave functions of the determinantal form (2), is greatly simplified if the one-electron wave functions are taken to be mutually orthogonal and normalized. If the form (3) is taken for the one-electron wave functions, those ψs for which l, m, or s is different are orthogonal on account of the properties of the spherical harmonics, or because of the spin functions. Those for which l, m and s are the same but n different are not orthogonal. We can, however, replace these one-electron wave functions by linear combinations which are orthogonal, and since this leaves the determinant unaltered the values of the integrals will not change. The method of constructing one-electron orthogonal wave functions out of non-orthogonal has been described by McDougall[8] and involves the radial wave functions P only.

We shall denote by P_0 the orthogonal radial wave functions obtained from the non-orthogonal self-consistent-field radial wave function P_s, and shall assume throughout the theoretical discussion that all wave functions are normalized. P_0

§ 3. FORMULA FOR THE ENERGY

The energy E of the stationary state Ψ is given by E

$$E = \int \Psi H \Psi^* d\tau \qquad \ldots\ldots(4),$$

provided

$$\int \Psi \Psi^* d\tau = 1 \qquad \ldots\ldots(5).$$

Slater[5] has given a formula for the energy. He assumes that Ψ has the determinantal form (2) and that the ψs are mutually orthogonal and of the form (3). He restricts his work in that he assumes also that all the electrons move in precisely the same field. Hartree and Black[9] removed this restriction and gave the modification of Slater's result in a form which applies to the case where the radial wave functions are obtained by the method of the self-consistent field.

Adopting Slater's notation, let us write

$I(\alpha)$ $$I(\alpha)=-\frac{1}{2}\int P_0(\alpha/r)\left[\frac{d^2}{dr^2}+\frac{2N}{r}-\frac{l_\alpha(l_\alpha+1)}{r^2}\right]P_0(\alpha/r)\,dr$$

$F_k(\alpha\beta)$ $$F_k(\alpha\beta)=\int\int P_0^2(\alpha/r)\,P_0^2(\beta/r_1)\,r_a^k/r_b^{k+1}\,dr\,dr_1=\int\frac{Y_k(\alpha\alpha/r)}{r}P_0^2(\beta/r)\,dr$$

$G_k(\alpha\beta)$ $$G_k(\alpha\beta)=\int\int P_0(\alpha/r)\,P_0(\beta/r)\,P_0(\alpha/r_1)\,P_0(\beta/r_1)\,r_a^k/r_b^{k+1}\,dr dr_1$$
$$=\int\frac{Y_k(\alpha\beta/r)}{r}P_0(\alpha/r)\,P_0(\beta/r)\,dr \qquad \text{.....(6),}$$

r_a, r_b where r_a and r_b are respectively the smaller and larger of r and r_1, and all the integrations are from 0 to ∞.

Then the modified form of Slater's result for the energy is

$$E=\sum_\alpha I(\alpha)+\sum'_{\alpha\beta}\sum_k a_k F_k(\alpha\beta)-\sum''_{\alpha\beta}\sum_k b_k G_k(\alpha\beta) \qquad \text{.....(7),}$$

Σ, Σ', Σ'' where Σ is the sum over all electrons, Σ' over all pairs of electrons and Σ'' over
a_k, b_k pairs with parallel spins. The coefficients a_k and b_k are certain definite integrals involving spherical harmonics and have been tabulated by Slater in his paper.

McDougall[8] has applied this result to the calculation of the optical terms of an atom with one series electron. The method is to neglect the perturbation of the core of the atom by the series electron, so that we may consider the energy of the optical term λ to be the difference between the energies of the atom and of the
E_λ ion. The energy E_λ of the optical term is thus given by

$$E_\lambda=I(\lambda)+\sum_\alpha J(\alpha;\lambda)-\sum_{\alpha\,||\,\text{spin}} K(\alpha;\lambda) \qquad \text{.....(8),}$$

where the sums are now over the core electrons only.

In order to calculate the energies of the optical terms our procedure is, therefore, first to obtain the radial wave functions P_s; then by linear combination to construct the orthogonal radial wave functions P_0; to calculate the integrals I, F and G, and finally to substitute in (8) to get the corresponding E.

We shall proceed to describe the necessary calculations for the states $(2s)$, $(2p)$, $(3p)$ and $(4p)$ of the series electron of lithium.

§ 4. THE CALCULATION OF THE ENERGIES OF THE OPTICAL TERMS OF LITHIUM

Hargreaves[7] used Hartree's method of the self-consistent field to obtain approximate radial wave functions P_s, for the series electron of lithium in the states $(2s)$, $(2p)$, $(3p)$ and $(4p)$.† The core was assumed to be unperturbed by the series electron, and accordingly the same field, namely that of the lithium ion, was used for all the states. The author has calculated the P_ss for the core electrons $(1s)^2$

† The author is indebted to Mr Hargreaves for the loan of these data.

by the same method, as these were required for the construction of the orthogonal wave functions.

The process of approximation to the self-consistent field of the $(1s)^2$ group was carried out until the maximum difference between the estimated and calculated contribution to Z† from this group was 0·008. The field for the ion was found to agree with Hargreaves's published value within a maximum difference of 0·8 per cent, whereas Wilson[10], using the variation method with a variation function containing four parameters, obtained a maximum difference of 2 per cent.

Table 1

r	$P_0(1s)$	$P_0(2s)$	$P_0(2p)$	$P_0(3p)$	$P_0(4p)$
0·0	0·0000	0·0000	0·0000	0·0000	0·0000
0·1	0·6884	0·0676	0·0028	0·0017	0·0011
0·2	1·0313	0·1012	0·0099	0·0066	0·0040
0·3	1·1670	0·1135	0·0201	0·0133	0·0079
0·4	1·1808	0·1118	0·0320	0·0192	0·0128
0·5	1·1264	0·0998	0·0465	0·0275	0·0182
0·6	1·0358	0·0769	0·0620	0·0391	0·0243
0·8	0·8190	0·0306	0·0962	0·0561	$0·0372_5$
1·0	0·6129	−0·0296	0·1317	0·0769	0·0509
1·2	0·4517	−0·0980	0·1673	0·0981	0·0631
1·4	0·3207	−0·1647	0·2059	0·1179	0·0775
1·6	0·2244	−0·2279	0·2414	$0·1365_5$	0·0894
1·8	0·1552	−0·2859	0·2747	0·1531	0·0998
2·0	0·1080	−0·3376	0·3056	0·1676	0·1085
2·4	0·0489	−0·4184	0·3574	0·1910	0·1203
2·8	0·0217	−0·4703	0·3972	0·1988	0·1238
3·2	0·0094	−0·4965	0·4230	0·1983	0·1196
3·6	0·0040	−0·5018	0·4370	0·1874	0·1076
4·0	0·0002	−0·4917	0·4403	$0·1680_5$	0·0912
5	—	−0·4260	0·4155	0·0894	0·0300
6	—	−0·3312	$0·3616_5$	−0·0052	0·0368
7	—	−0·2427	0·2979	−0·1013	0·0975
8	—	−0·1706	$0·2357_5$	−0·1844	0·1410
9	—	−0·1161	0·1811	−0·2480	0·1629
10	—	−0·0772	0·1364	−0·2913	0·1633
11	—	−0·0488	0·1010	$-0·3140_5$	0·1417
12	—	−0·0323	0·0745	−0·3200	0·1104
13	—	−0·0202	0·0554	−0·3139	0·0659
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26	—	—	0·0003	−0·0461	0·2324
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35	—	—	—	—	0·1149
40	—	—	—	—	0·0622
50	—	—	—	−0·0001	0·0142
60	—	—	—	—	0·0026
70	—	—	—	—	0·0004
80	—	—	—	—	0·0000

$S(1s; 2s) = 0·0837$.

† I.e. *effective nuclear charge*, or number such that the charge Ze placed at the nucleus would give the same field at the point as is actually found.

For lithium only the $(2s)$ wave function need be made orthogonal to the $(1s)$ wave function. The p functions are already orthogonal to the s functions and to each other. For the normalized functions we take†

$$\left.\begin{aligned} P_0(1s/r) &= P_s(1s/r) \\ P_0(2s/r) &= [P_s(2s/r) - S(1s;\,2s)\,P_s(1s/r)]/[1-S^2(1s;\,2s)]^{\frac{1}{2}} \\ P_0(np/r) &= P_s(np/r) \qquad (n=2,\,3,\,4) \end{aligned}\right\} \quad \ldots\ldots(9),$$

$S(1s;\,2s)$ where $$S(1s;\,2s) = \int_0^\infty P_s(1s/r).P_s(2s/r)\,dr.$$

The value $S(1s;\,2s)$ is given at the foot of the tables of P_0; see table 1.

The self-consistent and orthogonal wave functions are exhibited graphically in figure 1. It will be seen that the $(2s)$ orthogonal wave function differs considerably from the non-orthogonal wave function up to $r=2$. Beyond $r=2$ the non-orthogonal and orthogonal curves are identical. The difference between the self-consistent-field radial wave function $P_0(1s)$ and the radial wave function P_f obtained from Fock's equations, $P_f(1s)$, is too small to be shown in figure 1.

The I integrals. The radial wave functions P_s have been calculated by the method of the self-consistent field, so that they are solutions of equations of the form

$$\left\{-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\frac{l_\alpha(l_\alpha+1)}{r^2}\right\}P_s(\alpha/r) = \{v_\alpha - \tfrac{1}{2}\epsilon_\alpha\}\,P_s(\alpha/r) \quad \ldots\ldots(10),$$

in Hartree's notation[4].

From equations (6), (9) and (10) it follows that

$$\begin{aligned} I(2s) &= \int_0^\infty P_0(2s/r)\,[(v_{2s}-3/r-\tfrac{1}{2}\epsilon_{2s})\,P_s(2s/r) \\ &\qquad - S(2s;\,1s)\,(v_{1s}-\tfrac{1}{2}\epsilon_{1s}-3/r)\,P_s(1s/r)]\,\frac{dr}{\{1-S^2(1s;\,2s)\}^{\frac{1}{2}}} \\ &= -\tfrac{1}{2}\epsilon_{2s}+\int_0^\infty P_0^2(2s/r)\,(v_{2s}-3/r)\,dr \\ &\qquad + \frac{S(1s;\,2s)}{\{1-S^2(1s;\,2s)\}^{\frac{1}{2}}}\int_0^\infty \{v_{2s}-v_{1s}\}\,P_0(1s/r)\,P_0(2s/r)\,dr \quad \ldots\ldots(11). \end{aligned}$$

Similarly, $$I(np) = -\tfrac{1}{2}\epsilon_{np}+\int_0^\infty P_0^2(np/r)\,\{v_{np}-3/r\}\,dr \qquad (n=2,\,3,\,4).$$

Since the field for the ion was used to calculate the series-electron wave functions,

$$v_{\text{ion}} = v_{2s} = v_{np}$$

so that $$I(np) = -\tfrac{1}{2}\epsilon_{np}+\int_0^\infty P_0^2(np/r)\,\{v_{2s}-3/r\}\,dr \quad \ldots\ldots(12).$$

It is not necessary to calculate the individual integrals in equations (11) and (12), as the integrals occurring in the F functions may be grouped with them, and a simplification results.

† Cf. McDougall, reference (8), p. 563.

Energies of $(2s)$ *and* (np) *states.* From equation (8)

$$E(2s) = I(2s) + 2F_0(1s, 2s) - G_0(1s, 2s)$$

$$= -\tfrac{1}{2}\epsilon_{2s} + \int_0^\infty P_0^{\,2}(2s/r)\{v_{2s} - 3/r\}\,dr + \frac{S(1s; 2s)}{\{1 - S^2(1s; 2s)\}^{\frac{1}{2}}}\int_0^\infty (v_{2s} - v_{1s})\,P_0(1s)\,P_0(2s)\,dr$$

$$+ 2\int_0^\infty \frac{Y_0(1s, 1s/r)}{r}\,P_0^{\,2}(2s/r)\,dr - G_0(1s, 2s) \quad \ldots\ldots(13),$$

by substitution from equations (6) and (11).

Now if an exact solution of the self-consistent field has been obtained

$$(rv_{2s}) = [Z_p]_{\text{ion}} = 2\,[Z_p]_{1s} + 1,$$

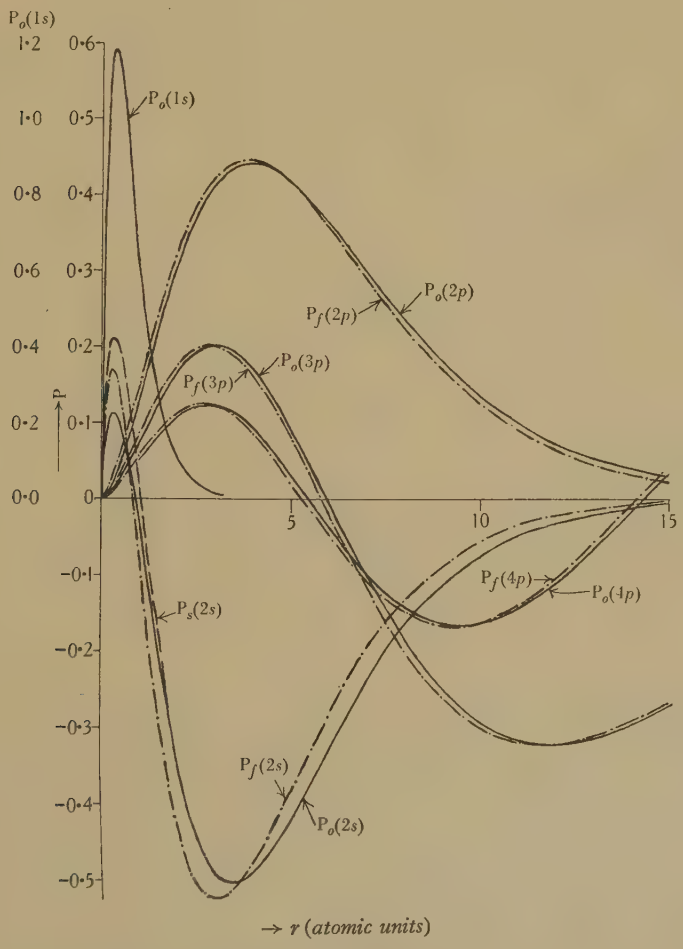

Figure 1. Normalized radial wave functions for lithium. — — — from solutions of the equations of the self-consistent field (P_s). ——— from the solutions of the self-consistent field but made orthogonal to 1*s* wave function (P_0). —·—·— from solutions of Fock's equations (P_f). The scale of the ordinate of the 1*s* radial wave function is half that of the other radial wave functions.

and $Y_0(1s, 1s/r) = 1 - [Z_p]_{1s}$,† so that

$$E(2s) = -\tfrac{1}{2}\epsilon_{2s} - \int_0^\infty \left[-\frac{S(1s; 2s)}{\{1 - S^2(1s; 2s)\}^{\frac{1}{2}}}(v_{2s} - v_{1s}) + \frac{Y_0(1s, 2s/r)}{r} \right] P_0(1s/r)\, P_0(2s/r)\, dr \qquad \ldots\ldots(14).$$

The integral in this last equation will be referred to as *the contribution to the energy* $E(2s)$.

Similarly, the integral in $I(np)$ cancels out with the contribution from the Fs, and the values of the energies are

$$E(np) = -\tfrac{1}{2}\epsilon_{np} - \tfrac{1}{2}\, G_1(1s, np),$$

where

$$G_1(1s, np) = \int_0^\infty \frac{Y_1(1s, np/r)}{r}\, P_0(1s/r)\, P_0(np/r)\, dr \qquad \ldots\ldots(15).$$

The ϵs are the energy parameters of the self-consistent field, and have been given by Hargreaves[7]. The corrections to these consist of the additional terms in equations (14) and (15). The method of calculating Y_0 and Y_1 has been fully described in Hartree and Black's paper[9] and reference should be made to that paper for further details.

Table 2 gives the numerical values of the contributions to the energies and the total energies in accordance with the relations (14) and (15).

Table 2. Energies of optical terms of lithium

Term	ϵ	$G_1(1s, np)$	Contributions to $2E$	$2E$ orthogonal wave functions	$2E$ Fock wave functions	$2E$ observed values
$1s$	5·570	—	—	—	—	—
$2s$	0·3560	—	0·0283	0·3843	0·3934	0·3964
$2p$	0·2518	0·0078	0·0052	0·2570	0·2574	0·2606
$3p$	0·1117	0·0023	0·0015	0·1132	0·1135	0·1145
$4p$	0·0628	0·0010	0·0006	0·0634	0·0636	0·0640

The unit of energy is e^2/a_0.

§ 5. FOCK'S EQUATIONS

The method of the self-consistent field neglects exchange effects. If we wish to include these exchange terms and so obtain a better approximation to the wave function of the atom, we must use the determinantal form (4) consisting of central-field one-electron wave functions (5) for the wave function of the whole atom. The differential equations which must be satisfied in this case by the generalized self-consistent-field radial wave functions P_f have been obtained by Fock[11], who applied the variation principle. The method of deriving these equations is to make

$$E \text{ equal to } \int \Psi H \Psi^* d\tau$$

† Cf. McDougall, reference (8), p. 573.

a minimum for small variations of the radial wave functions. The equations for sodium[12] and for lithium† have been solved numerically by Fock and Petrashen.

The Fock wave functions† are drawn in figure 1, and it is easy to see that the differences between $P_f(2s)$ and both $P_s(2s)$ and $P_0(2s)$ is considerable. The $(2s)$ wave function of the self-consistent field, $P_s(2s)$, as an approximation to the Fock $(2s)$ wave function $P_f(2s)$, is just as good as, if not better than, the orthogonal self-consistent-field wave function $P_0(2s)$. This particular property Hartree[13] found also in the case of normal beryllium. For all the series electron wave functions, the Fock wave functions are in the neighbourhood of the origin numerically greater than the corresponding self-consistent-field functions.

§ 6. FORMULA FOR THE INTENSITIES

In order to compute the intensity of the transition of the series electron from the normal state to a higher state, we require to know the value of the Heisenberg matrices,

$$R=\int \Psi^* \sum_k r_k \Psi' \, d\tau \qquad (k=1, \ldots, n) \qquad \ldots\ldots(16), \qquad R$$

where Ψ, Ψ' are the normalized wave functions of the atom in the normal and excited states respectively. Ψ, Ψ'

We shall assume that the wave function of the atom is of the determinantal form (2); that all the one-electron wave functions are orthogonal and normalized; and the approximation that raising the series electron to a higher level leaves the other one-electron wave functions unaltered. Thus, we can put

$$\Psi=\frac{1}{\sqrt{(n!)}}\begin{vmatrix} \psi(\alpha/1) \ldots \psi(\rho/1) \\ \vdots \\ \psi(\alpha/n) \ldots \psi(\rho/n) \end{vmatrix} \quad \text{and} \quad \Psi'=\frac{1}{\sqrt{(n!)}}\begin{vmatrix} \psi(\alpha/1) \ldots \psi(\rho'/1) \\ \vdots \\ \psi(\alpha/n) \ldots \psi(\rho'/n) \end{vmatrix} \qquad \ldots\ldots(17),$$

where ρ denotes the series electron which is raised to the state represented by ρ'. ρ, ρ'

The orthogonality and normalizing conditions

$$\int \psi(\lambda)\,\psi(\mu)\,d\tau=\delta_\mu{}^\lambda \qquad \lambda, \mu=\alpha, \ldots \rho, \rho' \qquad \ldots\ldots(18),$$

reduce the integral in equation (16) to

$$\frac{1}{\sqrt{(n!)}}\int \sum_k r_k \left\{\sum_P P.\psi^2(\alpha/1)\,\underset{\text{omitting } k}{\psi^2(\beta/2)} \ldots \psi^2(\pi/n)\right\} \psi(\rho/k)\,\psi(\rho'/k)\,d\tau,$$

where P denotes the permutation of the coordinates among the one-electron wave functions. P

Hence,
$$R=\frac{1}{(n!)}\int \sum_k r_k .(n-1)!\,\psi(\rho/k)\,\psi(\rho'/k)\,d\tau$$
$$=\frac{1}{n}\int \sum_k r_k\,\psi(\rho/k)\,\psi(\rho'/k)\,d\tau$$
or
$$R=\int \psi(\rho).r.\psi(\rho')\,d\tau \qquad \ldots\ldots(19),$$

† These have been taken from Fock and Petrashen's work[27]. The author wishes to express his gratitude to Miss Petrashen for allowing him to use the figures previous to their publication.

which depends only on the one-electron wave functions of the series electron which is excited. It is to be remembered that this is only true when we assume that the excitation leaves the other electrons unperturbed.

If we now replace $\psi(\rho)$ and $\psi(\rho')$ by the central-field form (5), the integrals (19) consist of three portions; two of these depend upon θ and ϕ, and can be evaluated. We are then left with a single integral which is a function of the radial wave functions only.

We obtain finally,

$$\sum_{mm'} R^2_{nlm,\,n'l'm'} = \left(\int_0^\infty rP\,(nl/r)\,P\,(n'l'/r)\,dr\right)^2 \qquad \text{.....(20)},$$

where the Ps are orthogonal and normalized, and (nlm), $(n'l'm')$ are the quantum numbers of the states ρ and ρ'.

The oscillator-strengths, f values, are obtained from Sugiura's formula[2],

$\nu_{nl,\,n'l'}$

$$f_{nl,\,n'l'} = \frac{1}{3}\cdot\frac{1}{g_{nl}}\cdot\frac{\nu_{nl,\,n'l'}}{R_0}\sum_{mm'} R^2_{nlm,\,n'l'm'} \qquad \text{.....(21)},$$

g_{nl} where $g_{nl}=(2l+1)$ and is the statistical weight of the low-energy configuration (nl) and $\nu_{nl,\,n'l'}$ the wave-number of the line corresponding to the transition (nl) to

R_0 the higher configuration $(n'l')$. R_0 is the Rydberg constant.

After we have found a central field which gives a satisfactory representation of the energy levels, we may use the radial wave functions calculated from this field to compute the radial integrals $\int rP\,(nl/r)\,P\,(n'l'/r)\,dr$. From these we can calculate the oscillator-strengths, and the ratios of the oscillator-strengths may be compared with the experimental data.

The radial integrals for lithium, for which $n=2$, $l=0$, $n'=2$, 3, 4, $l'=1$, were calculated by numerical integration and their values when P is equal to P_s, P_0, and P_f are given in table 3, together with the corresponding values of ν and f. The

ν wave-numbers ν were taken as the differences between the negative energies of the states (nl) and $(n'l')$ except for the non-orthogonal self-consistent field where

Table 3. Calculated values of the oscillator-strengths or f numbers

	$\int_0^\infty rP\,(2s/r)\,P\,(np/r)\,dr$			$\left(\int_0^\infty rP\,(2s/r)\,P\,(np/r)\,dr\right)^2$		
2s–2p	−4·49	−4·515	−4·135	20·16	$20{\cdot}38_5$	17·10
2s–3p	0·3573	0·5375	0·1905	0·1276	0·2889	0·0363
2s–4p	0·3890	0·3586	0·1719	0·1512	0·1286	$0{\cdot}0295_5$
	(a)	(b)	(c)	(a)	(b)	(c)

ν in atomic units				f numbers		
0·1042	0·1273	0·1360	0·1358	0·7000	0·8650	0·7751
0·2443	0·2711	0·2799	0·2819	0·0104	0·0261	0·0034
0·2932	0·3209	0·3298	0·3324	0·0147	$0{\cdot}0137_5$	0·0032
(a)	(b)	(c)	Observed	(a)	(b)	(c)

(a) Calculated from non-orthogonal radial wave functions ($P=P_s$).
(b) Calculated from orthogonal radial wave functions ($P=P_0$).
(c) Calculated from Fock radial wave functions ($P=P_f$).

they are the differences between the energy parameters ϵ. The experimental values were not used.

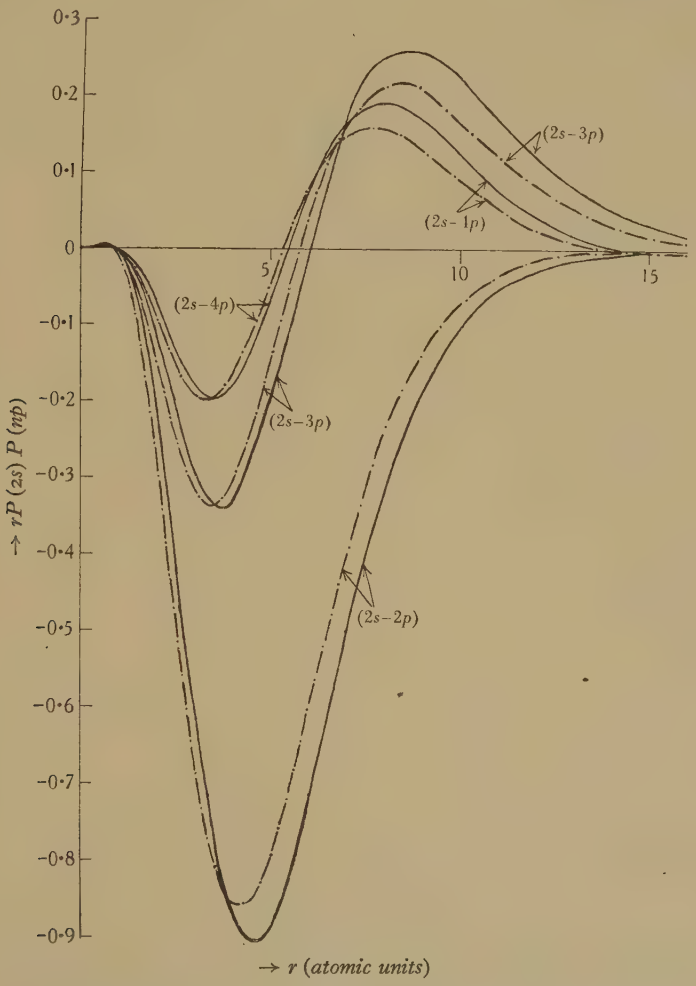

Figure 2*a*. The variation of $rP\,(2s)\,P\,(np)$. ——— for orthogonal self-consistent field radial wave functions P_0. —·—·— for Fock radial wave functions P_f.

Considerable care has to be taken in the calculation of $\int rP\,(2s/r)\,P\,(3p/r)\,dr$ and $\int rP\,(2s/r)\,P\,(4p/r)\,dr$ as the positive and negative contributions to these integrals are very nearly equal. A small change, therefore, in the wave functions has quite a large effect on the value of the integrals and correspondingly on the f numbers. Figures 2*a* and 2*b* show the variation of $rP\,(nl/r)\,P\,(n'l'/r)$ with r.

§ 7. RESULTS AND DISCUSSION

For the energy parameter for the (1*s*) state the value obtained by the author by applying the method of the self-consistent field was 5·570 in atomic units. Bethe[14] in calculating the electron distribution of Li^+ by the Hylleraas[15] or

variation method obtained 5·589, whilst the experimental value of the ionization potential of Li^+ is 5·560 according to Bacher and Goudsmit[16] and 5·564 according to Edlén and Ericson[17].

The other theoretical calculations of the normal state of Li and Li^+ are those of Eckart[18], Guillemin and Zener[19], and Wilson[10], who all employed the variation method with a determinant of the type (4) for the wave function of the whole atom. The one-electron wave functions were limited to a specified analytical form, Eckart using hydrogen-like wave functions with two parameters, Guillemin and

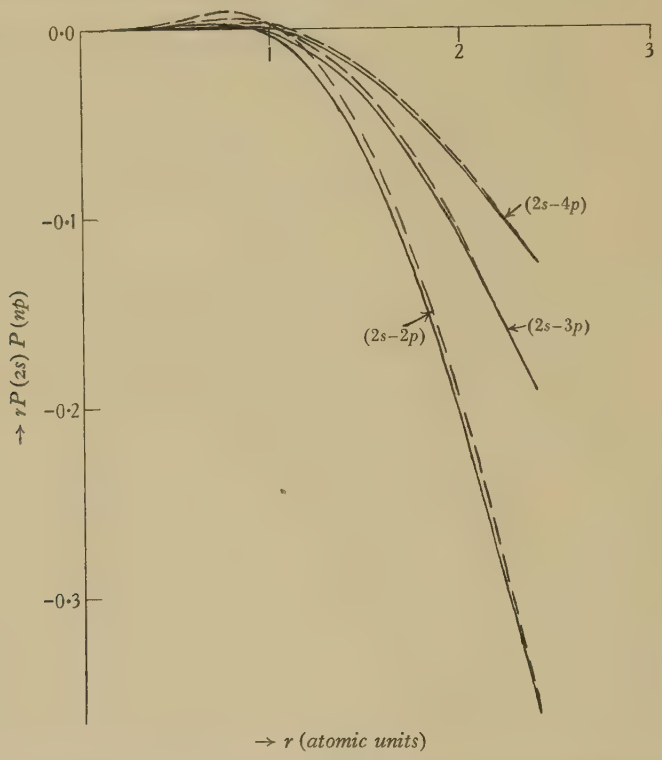

Figure 2*b*. The variation of $rP(2s)\,P(np)$. ——— for orthogonal self-consistent field radial wave functions P_0. — — — for non-orthogonal self-consistent field radial wave functions P_s.

Zener three parameters, and Wilson four parameters. Zener[20] and Slater[21] have proposed slightly simpler functions than Eckart's. The results for the energy of the (2*s*) state by these methods, as given by Wilson[10], are included in table 5. James and Coolidge[22] have recently obtained the value 0·3950 by an extended Hylleraas method.

ϵ The improvement effected in the E values over the energy parameters ϵ of the self-consistent field by the inclusion of the interchange terms of the Slater formula is very satisfactory. An even greater improvement is obtained by using the solutions of the Fock equations—see columns 2, 5, 6 and 7 of table 2. The greatest differences between the self-consistent field, orthogonal self-consistent field, Fock, and observed values of the energies are of the order of 10, 3 and 1 per cent respectively.

McDougall has pointed out[8] that the self-consistent-field wave functions for the series electron outside the core are better approximations than those obtained by making the wave functions fit the observed ϵ. It seems possible, therefore, that, since the main contributions to the fs come from outside the core, the fs calculated from wave functions made to fit the observed ϵ are the least accurate, those from the self-consistent field or orthogonal self-consistent field are more accurate, and those from the Fock equations are the most accurate.

Calculations of the f numbers for the first two lines of the principal series ($2s$–np) of lithium have been made by Trumpy[23] by using radial wave functions based on an empirical field of force for the atom. He obtained this field from the observed term-values by a method based on the old quantum theory (Sugiura's method). Later[24] he revised the work, using a Hartree field but one so modified that the wave functions fitted the boundary conditions for the observed ϵ. In table 4 the experimental values for the ratios of the f numbers, measured by Trumpy[25] and by Filippov[26], are compared with the calculated values. The calculated values are those calculated in this paper together with those obtained by Trumpy[23, 24].

Table 4. Relative values of f numbers

	Calculated values					Observed values	
	Self-consistent field (Hargreaves)	Orthogonal self-consistent field (author)	Fock wave functions (author)	Trumpy 1928	Trumpy 1930	Trumpy	Filippov
f_{2s-2p}/f_{2s-3p}	67·3	33·1	222	11·2	136	—	136·5
f_{2s-3p}/f_{2s-4p}	0·71	1·90	1·05	3·29	1·17	1·2	1·15
f_{2s-2p}	0·7	0·8650	0·7751	0·7230	0·7501	—	—

It appears that Trumpy's latest results are in close agreement with Filippov's experimental values, but it is doubtful, on account of what has been said above, whether Trumpy's results are more correct than those calculated in this paper. However, it seems certain that Hargreaves's result, which would make the third line stronger than the second, is in error. The radial integral ($2s$–$3p$) of the non-

Table 5. Energies of $1s$ and $2s$ states. Comparison of theoretical and observed values. (The unit of energy is $2e^2/a_0$)

$1s$-state		$2s$-state	
Energy parameter; author*	5·570	Energy parameter; Hargreaves[7]*	0·3560
Bethe[14]*	5·589	Orthogonal self-consistent field; author*	0·3843
Edlén and Ericson[17]†	5·564	Fock*	0·3934
Bacher and Goudsmit[16]†	5·560	Wilson[10]*	0·3934
		Guillemin and Zener[19]*	0·3912
		Slater[21]*	0·3906
		James and Coolidge[22]*	0·3950
		Bacher and Goudsmit[16]†	0·3964

* Theoretical value. † Observed value.

orthogonal self-consistent field is less than the radial integral ($2s$–$4p$). This does not occur in either the orthogonal self-consistent field or the Fock case; see table 4.

In conclusion, it is to be noted that for numerical in contrast to theoretical work, it is more convenient to use unnormalized wave functions (preferably those with the same dP/dr at $r=0$ for the same l) throughout, and to divide by the normalizing factors at the end of the calculations. Although all the wave functions quoted in this paper are given in the normalized form, nearly all the calculations were made with unnormalized functions, and the results were subsequently normalized by means of the appropriate factors.

§ 8. ACKNOWLEDGMENTS

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REFERENCES

(1) Einstein, A. *Phys. Z.* **18**, 121 (1917).
(2) Schrödinger, E. *Ann. Phys.*, Lpz., **80**, 437 (1926).
Sugiura, Y. *J. Phys. Radium*, **8**, 113 (1927).
Kupper, A. *Ann. Phys.*, Lpz., **86**, 511 (1928).
(3) Dirac, P. A. M. *Proc. roy. Soc.* A, **114**, 243 (1927).
(4) Hartree, D. R. *Proc. Camb. phil. Soc.* **24**, 89 (1928).
(5) Slater, J. C. *Phys. Rev.* **34**, 1293 (1929).
(6) Fock, V. *Z. Phys.* **61**, 126 (1930).
(7) Hargreaves, J. *Proc. Camb. phil. Soc.* **25**, 75 (1928).
(8) McDougall, J. *Proc. roy. Soc.* A, **138**, 550 (1932).
(9) Hartree, D. R. and Black, M. M. *Proc. roy. Soc.* A, **139**, 311 (1933).
(10) Bright Wilson, E. jr. *J. chem. Phys.* **1**, 210 (1933).
(11) Fock, V. *Z. Phys.* **81**, 195 (1933).
(12) Fock, V. and Miss Petrashen. *Phys. Z. Sowjet.* **6**, 368 (1934).
(13) Hartree, D. R. and Hartree, W. *Proc. roy. Soc.* A, **150**, 9 (1935).
(14) Bethe, H. A. *Z. Phys.* **57**, 815 (1929).
(15) Hylleraas, E. A. *Z. Phys.* **54**, 347 (1929).
(16) Bacher and Goudsmit. *Atomic Energy States* (McGraw Hill, 1932).
(17) Edlén, B. and Ericson, A. *Nature*, Lond., **124**, 688 (1929).
(18) Eckart, C. *Phys. Rev.* **36**, 878 (1930).
(19) Guillemin, V. and Zener, C. *Z. Phys.* **61**, 199 (1930).
(20) Zener, C. *Phys. Rev.* **36**, 51 (1930).
(21) Slater, J. C. *Phys. Rev.* **36**, 57 (1930).
(22) James, H. M. and Coolidge, A. S. *Phys. Rev.* **47**, 700 (1936).
(23) Trumpy, B. *Z. Phys.* **50**, 232 (1928).
(24) Trumpy, B. *Z. Phys.* **61**, 54 (1930); **66**, 720 (1930).
(25) Trumpy, B. *Z. Phys.* **57**, 787 (1929).
(26) Filippov, A. *Z. Phys.* **69**, 526 (1931).
(27) Fock, V. and Miss Petrashen. *Phys. Z. Sowjet.* **8**, 547 (1935).

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AN EXPERIMENTAL INVESTIGATION OF THE VALIDITY OF OHM'S LAW FOR METALS AT HIGH CURRENT-DENSITIES

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ABSTRACT. The paper describes experiments in which simultaneous measurements were made of the resistances of a gold conductor to a large direct current and a relatively small alternating current of radio frequency. At such frequencies the temperature of the conductor was found to remain practically constant in spite of the periodic nature of the heating effect produced by the alternating current. Thus any difference between the a.-c. and d.-c. resistances indicated a departure from Ohm's law, the skin effect being negligible. The experiments showed that the resistance of a gold conductor at constant temperature rises at very high current-densities and that the amount by which it rises increases with the temperature. The tests were made at current densities which reached 6×10^6 A./cm^2.

§ 1. INTRODUCTION

Many attempts have been made[1] to establish experimentally a deviation from Ohm's law* at high current-densities but it was not until 1922, when Prof. Bridgman[2] took up the matter, that any real progress was achieved. The great difficulty in making any crucial measurements has always been to distinguish between resistance changes due to temperature and those due simply to current density.

As a result of his investigations Bridgman claimed to have observed in the case of gold a definite deviation from Ohm's law at about a million ampères per cm^2, but the range of his measurements was very limited, and when in 1930 the author[3] repeated and extended Bridgman's work, introducing a number of refinements, he was driven to conclude that after the effect of heating had been properly eliminated the resistance became independent of the value of the current up to densities as high as two million A./cm^2.

The experiments herein described show that a deviation from Ohm's law does in fact exist at 2×10^6 A./cm^2, but at ordinary temperatures it is too small to have been detected with certainty by either Bridgman's or the author's previous apparatus. The present work demonstrates clearly that the resistance of a gold conductor at constant temperature rises at very high current-densities and that the amount by which it rises increases with the temperature.

* Formulated by the Munich physicist G. S. Ohm (1787–1854).

§ 2. PRINCIPLE OF EXPERIMENT AND DISCUSSION OF PREVIOUS WORK

The method of investigation employed was similar to that originally devised by Bridgman and consists in passing simultaneously through the conductor under test a relatively large d.c. and a small a.c. The potential-difference across the conductor is balanced in a simple bridge circuit firstly with a moving-coil galvanometer and secondly with a sensitive a.-c. detector. As one would expect, the balancing resistances are normally exactly the same for the d.c. and for the a.c. provided that the frequency is not so high as to introduce disturbances due to stray inductances, capacitances, etc. If, however, the density of the d.c. is raised sufficiently, the a.-c. resistance becomes slightly larger than the corresponding d.-c. resistance, the difference becoming smaller with an increase in the frequency of the a.c.

These facts can be explained by considering the {voltage, current} curve for the conductor under test and bearing in mind that the ordinary effect of heating will be to cause the voltage to rise more rapidly than the current at large values. Thus in figure 1 the d.-c. balance gives a resistance at the point W represented by the slope of the straight line OW, whereas the a.-c. balance with a low frequency gives a resistance at the same point represented by the slope of the line MWN or of the tangent to the curve at W. It is important to remember that in the bridge circuit a balance of potentials is obtained, and the value derived for the unknown resistance is that which would give an equal potential-drop in similar circumstances.

In order to get a very high current-density without employing a large current, and at the same time providing a sufficient cooling surface, it is necessary to use a conductor of small sectional area in the form of a thin film. The temperature of such a conductor responds readily to a change in the rate at which energy is dissipated in it, so that when the a.c. superposed on the d.c. is of comparatively low frequency, causing variations to take place about the point W on the curve as shown in figure 1, the corresponding changes in p.-d. would be expected to follow the static characteristic MWN.

The higher the frequency of the a.c. the smaller the fluctuations of temperature due to it, and the observed a.-c. resistance should approach the d.-c. resistance as the frequency rises. If the upward curvature of the {voltage, current} characteristic is due only to a rise of temperature, one would naturally expect that at radio frequencies the a.-c. resistance and the d.-c. resistance would become practically equal, the skin effect being negligible for the conductor employed. At an intermediate frequency the a.-c. resistance should correspond with the slope of a line such as $M'WN'$ in figure 1.

Plotting the difference between the a.-c. and the d.-c. resistances against the reciprocal of the frequency gives the curve[3] shown in figure 2, and the effect of the periodic heating and cooling of the conductor with the a.c. can obviously be eliminated if this curve is produced to cut the axis, the point of intersection corresponding with infinite frequency. For Ohm's law to be strictly true the extra-

polation must carry the curve, figure 2, through the origin, since in that case at infinite frequency there can be no difference between the a.-c. and d.-c. resistances. This is only another way of saying that for a conductor maintained at constant temperature the {voltage, current} characteristic is a straight line through the origin. On the other hand any departure from Ohm's law will be shown by an intercept such as *OH* on the vertical co-ordinate.

Employing this method to test the validity of Ohm's law must of necessity involve a certain amount of extrapolation of the curve shown in figure 2, and therein lies the weakness of the experiment. It was precisely this weakness that led Bridgman to interpret his results for gold and silver films as showing a definite deviation from

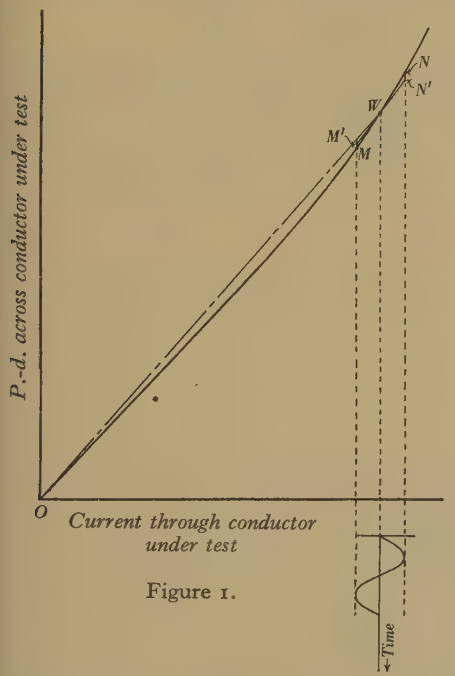

Figure 1.

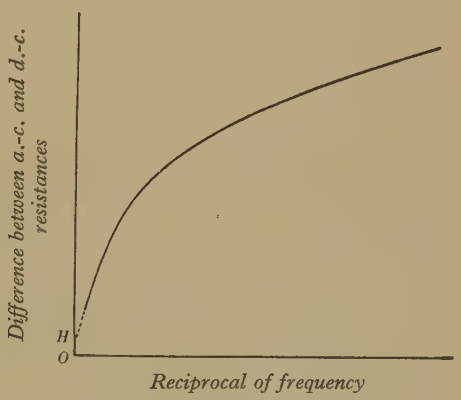

Figure 2.

Ohm's law at current-densities of the order of 10^6 A./cm.^{2} The superposed a.c. he employed was varied in frequency from 320 to 3750 c./sec., and with such low values covering so small a range it is impossible to rely with any certainty on the extrapolation process.

Realizing the importance attached to this point, the author in his previous investigation extended the frequency-range used up to 14,000 c./sec. and showed that in the case of gold at 2×10^6 A./cm.^{2} there was every indication of the difference between the a.-c. and d.-c. resistances becoming zero at an infinite frequency. There still remained, however, an element of doubt, and in order to come to a definite conclusion on this point the frequencies used in the present experiments were carried as high as $1{\cdot}15 \times 10^6$ c./sec., thus taking the measured values from which figure 2 is derived very near to the axis and reducing the extrapolation required to a minimum.

The magnitude of the a.c. passed through the conductor under test was shown previously[3] to be immaterial to the observations provided that it was small compared with the d.c. When the a.c. expressed as a fraction of the d.c. was varied from $\frac{1}{500}$ per cent up to about 0·5 per cent no measurable change occurred in the results obtained. In the present experiments the ratio adopted was between $\frac{1}{50}$ and $\frac{1}{20}$ per cent.

Both the d.c. and a.c. flow through the conductor during the measurement of the two resistances, so that no error is introduced by the slight increase in the average temperature due to the a.c.

§ 3. EXPERIMENTAL WORK

Description of apparatus. The general scheme of these experiments followed much the same lines as that previously adopted by the author, but the use of radio frequencies for the a.c. made necessary an entirely different construction of the apparatus. An outline of the bridge circuit is shown in figure 3, and figure 4 gives a more complete diagram of the arrangement of its various parts with the more important accessories.*

The balancing resistances in the bridge circuit were specially constructed to reduce as far as possible residual inductance, capacitance, skin effect, etc., and all components were enclosed in earthed metal screens. In each case a Eureka wire of 47 s.w.g. was arranged to form a narrow loop so that the lead and return conductors ran parallel with one another separated by a distance of 1 mm. The resistance P, figure 3, was fixed at a value of 42·1 Ω., whilst Q, which had a resistance of 71·8 Ω. (74·1 Ω. after reconstruction), was used as a potential-divider.

The sliding contact on Q was controlled by a screw movement as shown in figure 5. This piece of apparatus was very carefully made, to prevent any looseness between the rotary motion of the screw and the linear motion of the slider. The wire used was also selected as having a uniform cross-section and the assembly was calibrated to give a known transfer of resistance from one section of the slide wire to the other when the screw was turned through a certain angle. Thus an angular displacement of the operating handle amounting to 10 degrees corresponded with a resistance between tapping points of 0·0051 Ω. (0·00526 Ω. after reconstruction). The whole apparatus was enclosed in an earthed metal box and the conductor to the tapping point was brought out through a flexible metal tube to give the necessary freedom of motion.

A similar potential-divider was employed for the Wagner earthing-system, but in this case the slider was moved directly by hand instead of through the agency of a screw. When the bridge was balanced, the Wagner earthing-system enabled the detector points (a and b in figure 3) to be maintained at earth-potential without applying any actual earth connexion to the main circuit.

The wires joining the various components were made as short as possible, the

* Some useful hints on the construction of this radio-frequency bridge were obtained from the paper by D. W. Dye and T. Iorwerth Jones[4].

lead and return to each part of the network being kept together and jointly screened. In spite of these precautions it was found that the residual capacity was not quite balanced, and the variable air condensers C_1 and C_2 were employed to make a

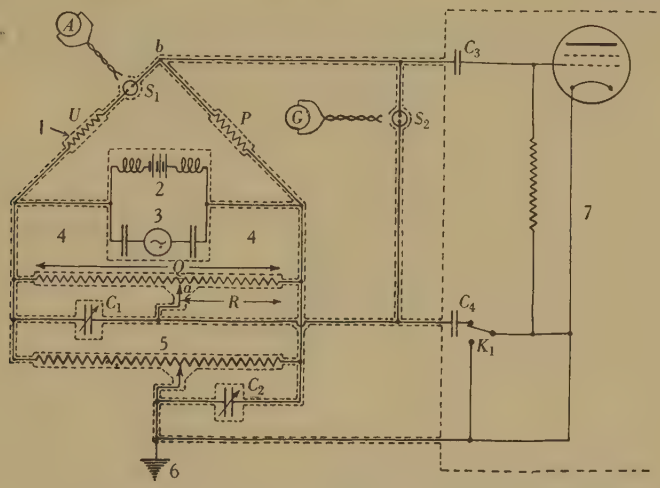

Figure 3. 1, conductor under test. 2, d.-c. supply. 3, a.-c. supply. 4, main bridge. 5, Wagner earthing system. 6, earth. 7, amplifier and detector.

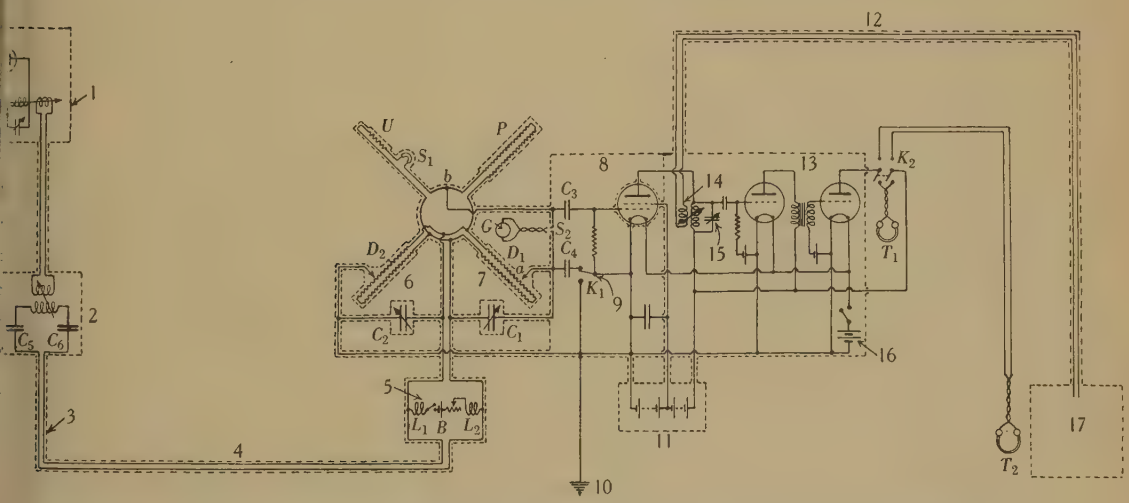

Figure 4. 1, calibrated variable frequency valve oscillator. 2, blocking condensers and coupling for h.-f. alternating current. 3, a.-c. supply to bridge. 4, 60 ft. of screened cable. 5, d.-c. supply to bridge. 6, Wagner earthing system. 7, main bridge system. 8, screen-grid h.-f. amplifier unit. 9, handle projects through screen. 10, earth. 11, S.G. and anode batteries. 12, 60 ft. of screened cable. 13, detector and l.-f. amplifier unit. 14, heterodyne input. 15, anode tuning. 16, filament battery. 17, auxiliary variable frequency valve oscillator (heterodyne).

suitable correction. A screened plug-socket S_1 was provided so that an ammeter could be connected in series with the conductor under test to measure the d.c. through it, or alternatively the socket could be short-circuited during the process of balancing the bridge.

Another plug-socket S_2 was connected to a sensitive moving-coil galvanometer to establish the condition for zero p.-d. between the detector points with d.c., and was left open-circuited when the heterodyne amplifier was employed to obtain the corresponding condition with the high-frequency a.c. The supply of current to the bridge was from an accumulator battery B feeding through choking coils L_1 and L_2 and from the calibrated variable-frequency valve oscillator O_1 coupled to the same pair of leads by means of blocking condensers C_5 and C_6.

Throughout the tests the a.c. employed was of the order of micro-amperes (about 7 μA.), ranging in frequency from 0·55 to 1·15 Mc./sec., and the balance of the bridge with this current was tested by using an auxiliary valve oscillator O_2 for heterodyning the output from a high-frequency amplifier connected to the points a, b, together with a detector, low-frequency amplifier and telephone receiver. Figure 4 shows the details of the arrangement.

The main high-frequency oscillator O_1 and the auxiliary one O_2 were situated about 60 ft. away from the bridge and from one another. To facilitate adjustment of the beat-frequency a pair of wires was taken from the output of the detector amplifier to another telephone receiver alongside the auxiliary oscillator. All parts of the equipment were carefully screened and a connexion was made to earth from the negative terminal of each filament battery.

The input to the grid of the high-frequency amplifier valve was by way of condensers C_3 and C_4, and the anode circuit of this valve was tuned to the particular frequency being employed. A single-pole change-over switch K_1 enabled a balance of the bridge to be made both with the potential-divider of the Wagner earth and the potential-divider of the main bridge.

The gold foils on which the tests were made, figure 6*a*, were mounted on the outside of a glass tube with shellac as a cement, the outer surface being exposed to the air. About midway between the terminal clips a narrow neck in the film was formed by cutting it with a razor blade while it was viewed through a microscope.

A stream of distilled water flowing transversely across the neck in the film was used in some of the tests for cooling purposes but, owing presumably to the formation of steam bubbles at the hottest point, fluctuations of resistance occurred which caused some difficulty in operating the bridge. Natural air cooling was found to give more stable conditions, and although the maximum current-density that could be employed was lower than with water cooling the difference was found to be much smaller than might be expected. The difficulty with the water was that the formation of a bubble caused a sudden rise in the temperature of the conductor approximating to the conditions prevailing when air was relied upon as the cooling medium.

In other tests a small resistance-grid made hot by a current passing through it was placed near the gold film, figure 6*b*, in order to provide supplementary heating. The film was for this purpose mounted on a quartz tube instead of a glass one.

Experiment showed that the best method of getting very high current-densities was to reduce the thickness of the foil and the width of the neck to a minimum.

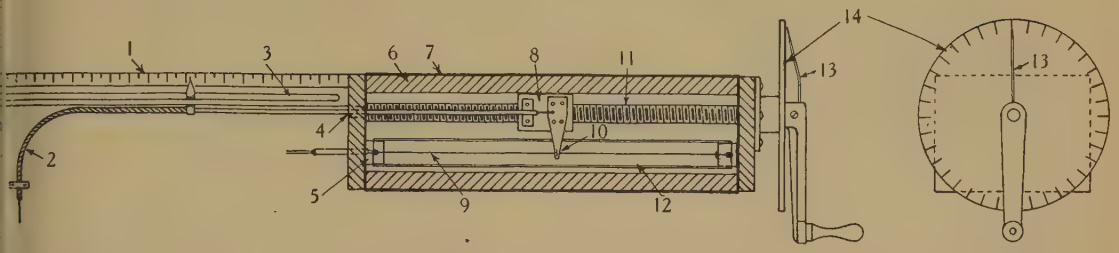

Figure 5. High-frequency potential divider for main bridge system. 1, scale. 2, screened flexible wire. 3, guide. 4, sliding fit. 5, plug to support end of glass tube. 6, wood. 7, metal screen. 8, ebonite support for slider. 9, 47 s.w.g. Eureka slide wire soldered to platinum deposited on ends of glass tube; wire returns on inside of glass tube. 10, slider. 11, screw, 26 threads per inch. 12, glass tube $\frac{3}{16}$ in. wall, $\frac{1}{2}$ in. inside diam. 13, pointer. 14, scale marked in degrees.

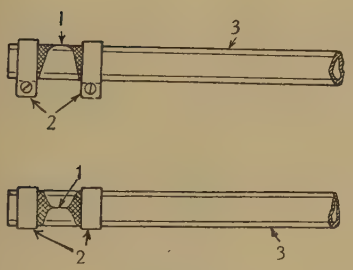

Figure 6*a*.

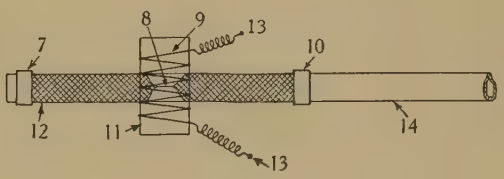

Figure 6*b*.

Figure 6*a* and *b*. Mounting for gold leaf forming conductor under test.

Figure 6*a*. Above: side elevation. Below: plan. 1, gold leaf cemented to glass tube with shellac and cut to form a narrow neck 0·5 mil. wide at this point. 2, copper clips forming terminals. 3, glass tube $\frac{9}{32}$ in. outside diam.

Figure 6*b*. 7, copper terminal clip. 8, narrow neck in gold leaf 0·5 mil. wide. 9, tungsten heater wire mounted on mica card. 10, copper terminal clip. 11, mica card. 12, gold leaf cemented to quartz tube with shellac. 13, electric heater terminals. 14, quartz tube.

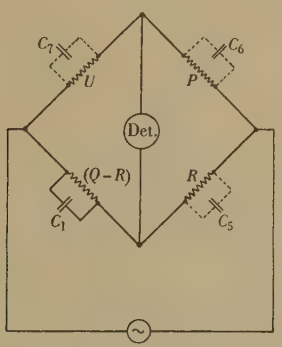

Figure 7.

The foils employed were prepared from ordinary gold leaf by continuing the beating process until the thickness had been reduced to 5×10^{-6} cm. This dimension was determined by weighing a sheet of the metal about 8 cm. square and assuming a density of 19·5 g./cm^3, a figure a little in excess of the normal, to allow for hammering. The width of the neck was measured under the microscope.

Procedure in making the measurements. The bridge, figure 4, was first balanced with a.c., the detector-amplifier and the heterodyne oscillator being used to give a suitable beat-frequency in the telephone receiver. The potential-dividers and variable condensers attached to the Wagner and main bridge systems respectively were adjusted alternately to give simultaneous balance for both positions of the switch K_1. With d.c. the condition for balance was indicated by the galvanometer G.

Theory of bridge circuit and calculations. With a small d.c. one would expect the balance of resistances in the main bridge as shown by the galvanometer and by the telephone receiver to be the same. This was in fact found to be the case with a.c. of audio frequency, but at radio frequencies the effective a.-c. resistance of the gold conductor became less than the corresponding d.-c. resistance. The difference was observed to be due mainly to stray capacities, and if these were neglected over the frequency range 0·55–1·15 Mc./sec. employed in these experiments there was always an apparent difference between the a.-c. and d.-c. resistances of the conductor under test, that difference becoming smaller as the current-density was increased.

It was found that the residual inductance of the main bridge circuit was relatively negligible and that the equivalent network could be represented with sufficient accuracy by figure 7. In terms of the symbols shown on the diagram the resistance of the conductor under test was therefore given by

$$U=\frac{P\,(Q-R)}{R}\left[\frac{1-\omega^2 C_5 C_7 UR}{1-\omega^2 C_1 C_6 P\,(Q-R)}\right]=\frac{P\,(Q-R)}{R}\,[1+x],$$

where ω is 2π times the frequency.

A bar being used to distinguish d.-c. quantities, the suffix o to indicate low values of current-density and the suffix h to indicate high values of current-density, then

$$\bar{U}_0=U_0 \quad \text{and} \quad x_0=\frac{Q\,(R_0-\bar{R}_0)}{\bar{R}_0\,(Q-R_0)}.$$

Any deviation from Ohm's law at high current-densities can be represented by Δ, equal to $U_h-\bar{U}_h$, and hence, since both x_0 and x_h are very small compared with unity,

$$\Delta=\frac{PQ}{\bar{R}_h}\left[\left(\frac{R_0-\bar{R}_0}{\bar{R}_0}\right)\left(\frac{Q-R_h}{Q-R_0}\right)^2-\left(\frac{R_h-\bar{R}_h}{\bar{R}_h}\right)\right].$$

The numerical values of Δ shown by the curves were calculated in each case from the above expression. Applying this theory to determine figures for C_1C_6 and C_5C_7 at different frequencies indicated that these quantities should be constant, and this conclusion was confirmed by experiment. At low current-densities the setting of C_1 remained practically unchanged.

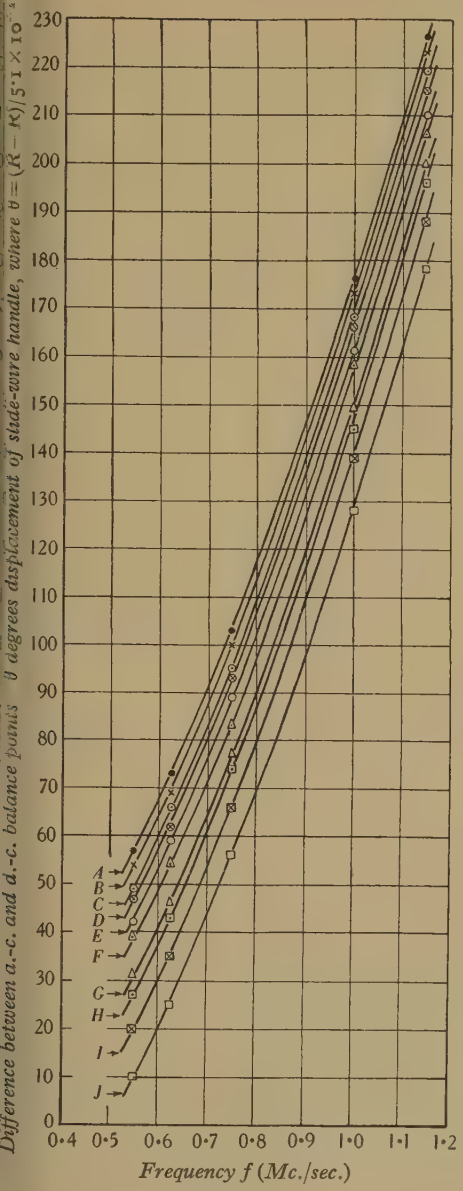

Figure 8.

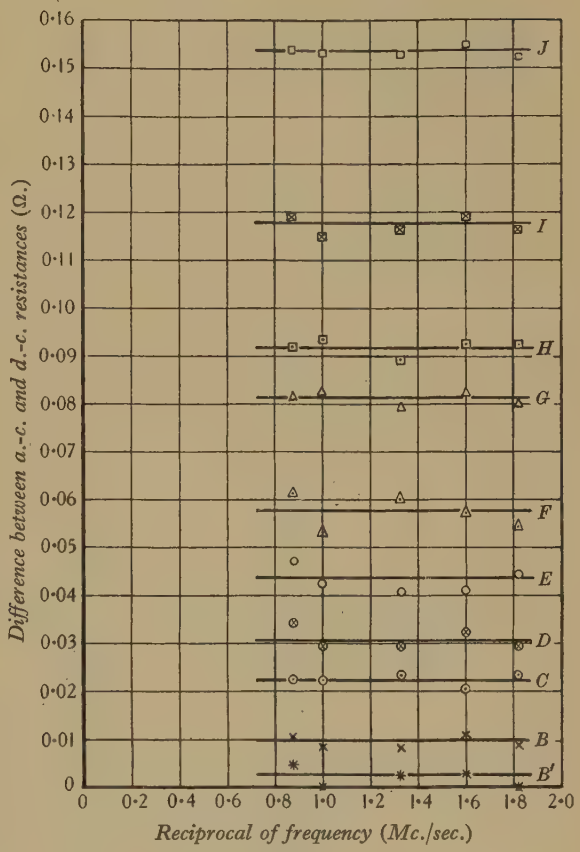

Figure 9.

Figure 8. Gold conductor, natural air cooling. *A*, $0{\cdot}24\times10^6$ A./cm.^{2} and $\bar{R}_0=23{\cdot}23\ \Omega$. *B*, $2{\cdot}44\times10^6$ A./cm.^{2} and $\bar{R}_h=23{\cdot}0\ \Omega$. *C*, $3{\cdot}23\times10^6$ A./cm.^{2} and $\bar{R}_h=22{\cdot}8\ \Omega$. *D*, $3{\cdot}58\times10^6$ A./cm.^{2} and $\bar{R}_h=22{\cdot}72\ \Omega$. *E*, $4{\cdot}02\times10^6$ A./cm.^{2} and $\bar{R}_h=22{\cdot}63\ \Omega$. *F*, $4{\cdot}41\times10^6$ A./cm.^{2} and $\bar{R}_h=22{\cdot}48\ \Omega$. *G*, $4{\cdot}96\times10^6$ A./cm.^{2} and $\bar{R}_h=22{\cdot}33\ \Omega$. *H*, $5{\cdot}2\times10^6$ A./cm.^{2} and $\bar{R}_h=22{\cdot}2\ \Omega$. *I*, $5{\cdot}67\times10^6$ A./cm.^{2} and $\bar{R}_h=21{\cdot}97\ \Omega$. *J*, $6{\cdot}15\times10^6$ A./cm.^{2} and $\bar{R}_h=21{\cdot}73\ \Omega$.

Figure 9. Gold conductor, natural air cooling. *B′*, $1{\cdot}65\times10^6$ A./cm.^{2} *B*, $2{\cdot}44\times10^6$ A./cm.^{2} *C*, $3{\cdot}23\times10^6$ A./cm.^{2} *D*, $3{\cdot}58\times10^6$ A./cm.^{2} *E*, $4{\cdot}02\times10^6$ A./cm.^{2} *F*, $4{\cdot}41\times10^6$ A./cm.^{2} *G*, $4{\cdot}96\times10^6$ A./cm.^{2} *H*, $5{\cdot}2\times10^6$ A./cm.^{2} *I*, $5{\cdot}67\times10^6$ A./cm.^{2} *J*, $6{\cdot}15\times10^6$ A./cm.^{2}

Conductor 5×10^{-6} cm. thick and $1{\cdot}27\times10^{-3}$ cm. wide.
Bridge resistances. $P=42{\cdot}1\ \Omega.$, $Q=71{\cdot}8\ \Omega.$

§ 4. EXPERIMENTAL RESULTS

The family of curves shown in figure 8 shows the differences between the a.-c. and d.-c. balances of the bridge as indicated by the position of the tapping-point on the slide wire Q, figure 3, when different frequencies are employed at a given current-density. The vertical intercept between any pair of curves is practically constant and therefore almost independent of frequency. This striking fact is borne out by the curves in figure 9, where the calculated difference between the a.-c. and d.-c. resistances of the conductor under test is plotted as a function of the reciprocal of the frequency. As the lines are horizontal one can confidently assume that the values of Δ represent a true deviation from Ohm's law.

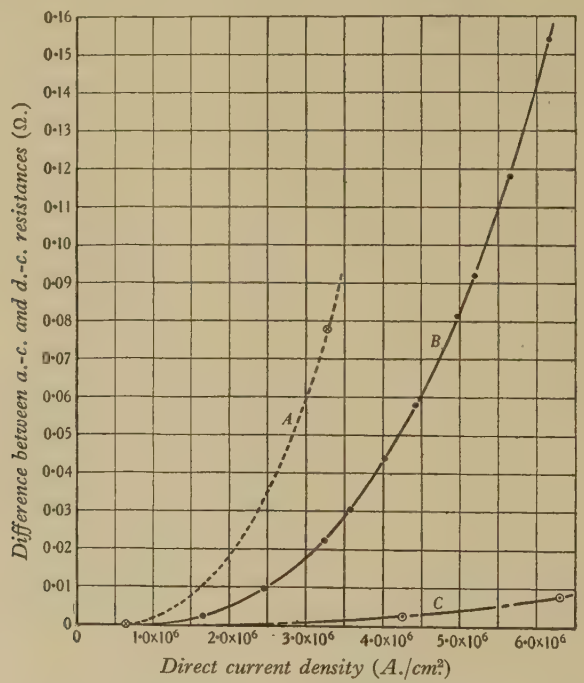

Figure 10. Gold conductor. *A*, conductor No. 2 with supplementary heating. *B*, conductor No. 1 with natural air cooling. *C*, conductor No. 1 with water cooling.

Curves similar to those shown in figures 8 and 9 were obtained when the conductor under test was cooled by a stream of distilled water flowing over it, but in this case Δ, although independent of frequency, was much smaller. Again, when the conductor under test was subjected to supplementary heating so that its temperature rose above that previously produced simply by the current through it, the difference between the a.-c. and d.-c. resistances, whilst remaining independent of frequency, became comparatively much larger.

Collected results and conclusion from experiments. In figure 10 the values of Δ signifying a true deviation from Ohm's law are plotted against current-density for different rates of cooling. The fact that the difference between the a.-c. and d.-c.

resistances is independent of frequency for radio values shows that the periodic heating and cooling effect of the a.c. has become negligible and that resistance-changes due to skin effect cannot have any material influence.

Unfortunately each curve does not represent constant temperature conditions since the rate of heating varies with the current density. Nevertheless there can be no doubt that the observed deviation from Ohm's law is a function both of current-density and of temperature. Thus one can confidently state that the resistance of a gold conductor at constant temperature rises at high current-densities, and the amount by which it rises increases with the temperature.

At low current-densities there is no deviation from Ohm's law even at comparatively high temperatures, but when the current-density is raised sufficiently for such a deviation to appear its magnitude increases rapidly with the temperature. After a certain minimum current-density has been reached there is in fact a possibility that the deviation from Ohm's law becomes entirely a function of temperature.

The present observations do not yield information from which a definite law governing the changes that take place could be deduced but the author hopes to probe further into the matter and if possible to establish an exact connexion between the quantities concerned.

§ 5. ACKNOWLEDGMENT

In conclusion the author desires to express his thanks to Prof. R. O. Kapp for placing the apparatus in the Pender Laboratory at his disposal.

REFERENCES

(1) (*a*) Clerk Maxwell, Everett J. D. and Schuster, A. *Brit. Assoc. Rep.* pp. 36–63 (1876).
(*b*) Lecher, E. *S.B. Akad. Wiss. Wien*, **116** (2*a*), 1, p. 49 (1907).
(*c*) von Traubenberg, H. Rausch. *Phys. Z.* **18**, 75 (1917).
(*d*) Wenner, F. *Phys. Rev.* (2) **15**, 531 (1920).
See also Thomson, J. J. *The Corpuscular Theory of Matter*, p. 54 (1907); Swann, W. F. G. *Phil. Mag.* **28**, 467 (1914); Compton, K. T. *Proc. Nat. Acad. Sci.* **12**, 548 (1926); Margenau, H. *Z. Phys.* **56**, 259 (1929) and **60**, 234 (1930).
(2) Bridgman, P. W. *Proc. Amer. Acad. Arts Sci.* **57**, No. 6, p. 131 (1922).
(3) Barlow, H. M. *Phil. Mag.* **9**, 1041–55 (1930).
(4) Dye, D. W. and Jones, T. Iorwerth. *J. Instn elect. Engrs*, **72**, 169 (1933).

DISCUSSION

Dr D. Owen. The subject of the paper is of great theoretical interest. In the conduction of electricity through a gas ionized at a constant rate Ohm's law fails when the current-density is sufficient to reduce appreciably the number of ions per unit volume, and saturation is reached at higher potential-gradients. Experiments on semi-insulating liquids appear to indicate a similar approach to a saturation current. The author's experimental dispositions in search for a similar effect in

metals, as described in this paper, seem admirably adapted to the purpose. An observed difference between the d.-c. resistance and the differential resistance obtained by superposition of a small alternating current should at first sight suffice to establish a departure from Ohm's law. But any alternating change of the temperature and consequently of the resistance of the conductor arising from the change in rate of evolution of heat produced by superposition of the alternating current tends to vitiate this conclusion. That such an effect is actually present in the experiments here described is suggested by the curves of figure 10, which indicate how considerable is the influence of the mode of cooling adopted. Calculation bears out the suggestion. For let I denote the large direct current, and $i_0 \sin pt$ the small superposed alternating current in the gold conductor. The increased rate of heating is $2Ii_0 \sin pt$, which will produce an oscillation of temperature of the same frequency, and consequently an addition $r_0 \sin pt$ to the resistance of the conductor. This change of resistance is doubtless very small, but it is important to note that the main current is flowing through it, with the result that virtually an e.m.f. $Ir_0 \sin pt$ is present in that arm of the bridge. The bridge is thus actually unbalanced by the very current required to supply the criterion. The d.-c. balance of course remains apparently unaffected, since the d.-c. indicator does not respond at the high frequency. The way out of this difficulty is clearly to use instead of gold a metal having a very low temperature coefficient of resistance, and it is to be hoped the author will find a means of making this step practicable.

Prof. W. Wilson suggested that the current might not be uniformly distributed in the film.

Dr L. Hartshorn. It is surprising that the author has been able to make films as thin as 0·05 μ., to weigh them, cut them to shape, and mount them on glass tubes. It would be interesting to have details of these processes. For instance, what tools are employed for the beating and subsequent manipulation? It might be worth while to make similar measurements on films prepared by sputtering, evaporation, precipitation, and electro-deposition. Probably films prepared by beating approximate more closely to the condition of metal in bulk, but it would be interesting to find out whether the observed property is characteristic of the method of preparation. If, as has been suggested, the peculiar properties of very thin films are characteristic of all surface molecules one might expect the same results with films prepared by all methods, but the question whether the property is also one of metal in bulk would still remain open. Similar experiments on films of various thicknesses might throw some light on this question.

Prof. H. Stansfield. Ohm's law may be divided into two parts: (1) the formula which Clerk Maxwell wrote $E = CR$ and described as a definition of R and (2) the information about R so defined gained from experiment, particularly as to how far R is independent of C. A President of this society who took a great interest in the history of physics, the late Prof. Sylvanus Thompson, maintained that Ohm's law would be true even if the resistance of a metallic conductor should be found to

vary with the current. I should say however that the general tendency in this country has been to move the title "Ohm's law" from (1) to (2), owing probably to the feeling that a definition should not be called a law. I incline the other way. I regard the definition as the essence of Ohm's contribution and the author's work described in this paper as a fresh tribute to its importance as well as an extension of our knowledge included in (2)..

Mr R. S. Whipple. Very thin films which have been chemically deposited are rarely homogeneous and may contain pin holes. I would suggest that a homogeneous film might perhaps be obtained if the author could devise a method of cathodic sputtering on to his surface, the latter being slowly rotated during the sputtering.

Author's reply. Dr Owen points out that any periodic change in the resistance of the conductor resulting from the superposed alternating current introduces a small alternating potential-difference which may invalidate the results obtained. This is undoubtedly one of the principal difficulties in connexion with the experiment, and indeed at comparatively low frequencies the heating and cooling effect referred to by Dr Owen does become one of the controlling factors. But I have shown that when the alternating current is very small and its frequency high the effect becomes negligible, as is indicated by the fact that the difference between the a.-c. and d.-c. resistances is then independent of frequency. In these circumstances the temperature of the conductor presumably remains substantially constant. Further experiments confirm this conclusion. They show that the difference between the a.-c. and d.-c. resistances becomes a function of frequency even at radio values, when the magnitude of the alternating current is sufficiently increased.

The observed departure from Ohm's law is exceedingly small and does not appear until the conductor is on the point of fusing. The figures recorded in the paper refer to a conductor having a resistance of about 96 ohms so that the largest value of Δ expressed as a percentage of this resistance is only about 0·15 per cent. Experiment indicates that the effect of temperature and method of cooling, on the value of Δ is accounted for by the change in the resistance of the conductor U and that Δ/U is independent of temperature, depending only upon the current-density. Thus a conductor of small resistance has a correspondingly small value of Δ for a given current density.

The suggestions of Dr Owen, Dr Hartshorn and Mr Whipple that similar experiments should be made on a conductor of low temperature coefficient and on films prepared by different methods are excellent ones and I hope to carry out a further investigation on those lines. In particular, graphite suggests itself as having a negative temperature coefficient and it can be readily prepared in a suitable form.

The process by which the gold conductors were made is referred to on page 556 of the paper. Raw hide was used to beat the metal down to the minimum thickness possible without destroying the continuity of the film. It was found that pure gold leaf would not stand as much beating as the gold alloy which is used commercially. This alloy was therefore employed in the experiments described. The film was

mounted on the glass by rolling the tube, made slightly sticky with a very thin layer of shellac, over the surface of the leaf. A narrow neck in the film was then formed by cutting it with a safety-razor blade, the operation being performed under a microscope. This gave an opportunity to select a homogeneous part of the film for the formation of the neck.

As regards Prof. Wilson's remark, I do not think there is any reason to expect the distribution of current in the film to vary under the conditions of the experiment.

Prof. Stansfield raises the interesting question—what is really meant by Ohm's law? My information leads me to agree with Prof. Stansfield that Ohm's contribution consisted in giving an accurate definition of the terms electromotive-force, current and resistance by introducing the relationship $I=E/R$. Ohm was guided in the mathematical work from which he originally deduced his famous "law" by analogy with the problem of heat-conduction, but he afterwards verified his theoretical conclusions by making a number of experiments with thermoelectric piles and observing the potential-differences between different points in an electric circuit. Later Davy, Pouillet, Becquerel, Kohlrausch, Gaugain and Branly all laboured at experimental investigations of Ohm's relationship, establishing so much confidence in its accuracy that it came to be regarded as a law of nature.

535·338.4:546.28

ULTRA-VIOLET BAND-SYSTEMS OF SiCl

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ABSTRACT. The emission spectrum of SiCl, produced in a tube discharge through a continuous flow of $SiCl_4$ vapour, has three systems of doublet bands degraded towards the further ultra-violet, the 0, 0 bands being at λλ 2942, 2924, λλ 2436, 2424, and λλ 2232, 2221. They are attributed to transitions B → X, C → X and D → X, where X is a double level with electronic separation 207·9 $cm.^{-1}$, $\omega_e = 531{\cdot}0$ and $x_e\omega_e = 2{\cdot}2$; B is a single level 34186·0 $cm.^{-1}$ above X with $\omega_{\frac{1}{2}} = 698{\cdot}7$; C is a close doublet 41234·8 and 41247·8 $cm.^{-1}$ above X with $\omega_e = 674{\cdot}2$ and $x_e\omega_e = 2{\cdot}2$; and D is a single level 45005·9 $cm.^{-1}$ above X, with $\omega_{\frac{1}{2}} = 663$. These figures are from band-head measurements only. Datta's analysis of the B → X system is confirmed, except in his identification of the 2,0 and 3,0 bands and his interpretation of observed isotope band-heads. With Datta's 2,0 and 3,0 bands are two groups of prominent bands between λ 2830 and λ 2770 not fitting into any of the three systems; their emitter may be a chloride of silicon other than SiCl.

§ 1. INTRODUCTION

Apart of the spectrum described in this paper was observed in 1913 in the glow produced by the interaction of $SiCl_4$ vapour and active nitrogen[1]. The whole of it was observed in 1923 in the uncondensed induction-coil discharge in $SiCl_4$ vapour flowing continuously through a discharge tube[2]. Low-dispersion spectrograms of the discharge were taken with a small quartz-prism instrument (Hilger's E 6) and some of the stronger bands were also photographed in higher dispersion (about 7·5 A./mm.) with a 2·4-m. concave grating. The spectrum was seen to consist of two somewhat similar parts A and B, one on either side of the AlCl band-system that resulted from the use of aluminium electrodes. Each part consisted of bands degraded to the further ultra-violet, i.e. opposite in direction to the SiO bands, which were present if residual air had not been entirely displaced by the $SiCl_4$ vapour. Parts A and B were regarded as two related band-systems, each having progressions of bands with common separations of about 525 $cm.^{-1}$ and regular variations of intensity. A constant separation, amounting to about 205 $cm.^{-1}$ in A and 195 $cm.^{-1}$ in B, was also recognized, but this did not suffice for the make-up of the usual Deslandres' arrangement of the band-heads; it was, in fact, the interval between the heads of sub-bands such as had been observed in other doublet band-systems but were not understood. The observed numerical relations have now proved to be significant for the vibrational analysis, which was not apparent at that time.

More recently A. C. Datta[3], using a 12,000-V. discharge through $SiCl_4$ vapour at about 2 mm. of mercury and a spectrograph of much bigger dispersion (Hilger's E 1), has shown that the stronger part A between λλ 3118 and 2772 does, indeed, consist of a doublet system in which the above 205 $cm.^{-1}$ represents an electronic separation—whether it is in the upper or in the lower state is undetermined—and the intervals of about 525 $cm.^{-1}$ pertain to the vibrational levels of the lower state, the upper state having a previously unrecognized interval of nearly 700 $cm.^{-1}$ Datta also observed that the sub-bands are themselves double-headed, with a separation of from 5 to 8 $cm.^{-1}$ between the heads P_1 and Q_1 in the lower-ν sub-band, and between P_2 and Q_2 in the higher-ν.* There are band-heads in this region, some of them very intense, which are not mentioned by Datta and cannot be included in his band-system; these will be discussed presently (p. 571). The analysis of the weaker part B between λλ 2600 and 2200 is recorded in the present paper. As will appear presently, part B consists, not of one system as previously supposed, but of two systems with the same lower state as the stronger system (or systems) forming part A. Although the common lower state cannot, from emission observations alone, be identified with the ground state, it will be denoted by X for the present, and the three systems (excluding the strong bands in part A mentioned above) will be referred to as the λ 2942 or B → X,† the λ 2436 or C → X and the λ 2232 or D → X systems; these wave-lengths apply to the least refrangible heads of the three 0,0 bands.

§ 2. EXPERIMENTAL

For the new observations an uncondensed discharge through continuously flowing $SiCl_4$ vapour has again been used; it is much more powerful than was possible on the former occasion[2]. The discharge tube is a suitably modified form of the water-cooled pyrex tubes used for other purposes by Dr R. W. B. Pearse and his collaborators in this laboratory. Its essential feature is the large cylindrical sheet electrodes whose outer surfaces are in contact over their whole area with the cylindrical walls of the water-cooled glass bulbs; the only parts of the tube not wholly immersed in a tank of running cold water are the extension carrying the quartz window, through which the column is viewed end-on, and the leads to the electrodes. For the electrodes and leads nickel is used in preference to aluminium in the present case in order to eliminate the AlCl band-system[2,6] mentioned above. The $SiCl_4$ vapour is admitted into one bulb, and the gaseous products of its decomposition in the discharge are pumped away from the other, each bulb having a side tube (with stop-cock) protruding vertically above the water for this purpose. A series of soda-lime tubes protects the oil pump, which runs throughout each

* It is convenient to retain Datta's empirical designations of the heads; they have no connexion with Mulliken's use of these symbols for the theoretical classification of the branches. The rest of the notation used in the present paper is that of this Society's *Report*[4].

† Dr Sponer in tabulating Datta's results for the λ 2942 system in the first volume of her recent book[5] also denotes the lower state by X and the upper state by B. The common lower state of a number of systems observed only in emission is now so often denoted by X in the literature, that it would be well to substitute another letter G for states which are *known*, either from absorption observations or from theoretical considerations, to be ground states.

exposure. The discharge carries a 50-c./sec. current of 0·25–0·4 A. from a 5-kW. 2400-V. transformer whose primary is supplied from 230-V. mains, a suitable resistance being inserted in each circuit. With a spectrograph similar to that used by Datta, whose exposure times were about 8 hours, this discharge requires only $1\frac{1}{2}$–$2\frac{1}{2}$ hours according to the spectral region to be measured. This instrument (Hilger's E 1) has been used for the λ 2942 system (dispersion 5·1–3·8 A./mm. in this region) and for the λ 2436 system (dispersion 3·1–2·1 A./mm.). In the latter case, since the bands are so far resolved into rotational structure as to cause uncertainty in the identification of some of the band-heads, a smaller quartz-prism instrument (a predecessor of Hilger's E 2, dispersion about 10–7 A./mm.) has also been used. Only the latter instrument has been used for the weakest system λ 2232 (dispersion 6·7–5·5 A./mm.). The plates used were Imperial Ordinary (some paraffined, some not), Ilford Ultra-violet (Q) and Eastman Ultra-violet.

As will be seen in figure 1, the present spectrograms show very little but the bands of SiCl and lines of Si, Ni and Cu.* The last-named, arising from impurity in the nickel electrodes, have been used as standards for wave-length measurement in parts of a spectrogram where the overlaps with the juxtaposed Fe arc standards happened to be not entirely satisfactory. The strongest bands of the SiO systems[2,4,8] are present but not troublesome. The N_2 Second Positive bands, three of which at λ 2976·7 (2, 0), λ 2962·1 (3, 1) and λ 2953·3 (4, 2) are the most prominent features of the spectrogram reproduced in Datta's paper, are not detectable in the present plates.

§ 3. ANALYSIS OF THE THREE SYSTEMS OF $^{28}Si^{35}Cl$

Results of measurements of band-heads in several spectrograms are set out for the three systems of the main molecule $^{28}Si^{35}Cl$ in table 1 with rough visual estimates of the relative intensities of the bands and the assigned values of the vibrational quantum numbers; the symbols used for naming the heads are those already allotted, in the λ 2942 system, by Datta, whose analysis of this system is substantially confirmed. The present observations yield, on the whole, slightly smaller and steadier values for the intervals Q_2–P_2, Q_1–P_1, P_2–P_1, and, like the rougher 1923 measurements[2], include a few more bands, some of which will be discussed presently (p. 571).

Table 2, which is a composite Deslandres arrangement of the wave-numbers of, and intervals between, the P_1 and P_2 heads, shows that the intervals in the v'' progressions are so nearly alike for the three systems as to suggest a common lower level. Denoting this by X and the upper levels by B, C and D, and accepting for the moment Datta's identification of the 2,0 and 3,0 band-heads in the λ 2942

* The presence of copper became very clear through the development of a blue glow, which was confined to edges of the electrodes when the tube was first used but almost filled the same tube when the discharge was passed after about a fortnight's disuse of the tube. The spectrum of the blue glow was photographed in about 8 minutes' exposure in the first order of a 2·4-m. concave grating (the grating mentioned on p. 563 in a newly-built Eagle mounting). It shows the stronger parts of the band-systems of CuCl[7,4] in considerable intensity.

Table 1. Data for band-heads of $^{28}Si^{35}Cl$

λ 2942 system, B → X; and other bands (p. 571)							
Intensity	v', v''	Band-head	Datta		Author		
			λ (air)	ν (vac.)	λ (air)	ν (vac.)	$\nu_{obs.} - \nu_{calc.}$
1	1, 5	P_1			3117·82	32064·4	−1·4
		Q_1			7·40	68·7	
0?	1, 5	P_2			3097·55	32274·2	+0·5
		Q_2			—	—	
2	0, 3	P_1	3085·56	32399·6	3085·61	32399·1	+1·8
		Q_1	—	—	5·13	404·2	
2*	1, 4	P_1			3068·75	32577·1	−2·1
		Q_1			7·97	85·4	
3	0, 3	P_2	3065·61	32609·5	3065·77	32608·8	+2·6
		Q_2	—	—	—	—	
2	1, 4	P_2			3049·26	32785·3	−1·8
		Q_2			8·78	90·5	
4	0, 2	P_1	3036·64	32921·9	3036·57	32922·3	+1·8
		Q_1	5·88	29·8	6·21	26·2	
6	1, 3	P_1	3020·54	33097·5	3020·51	33097·4	+0·4
		Q_1	19·90	104·1	0·08	102·1	
6	0, 2	P_2	3017·76	33127·5	3017·65	33128·7	+0·3
		Q_2	7·12	34·5	7·24	33·2	
4	1, 3	P_2	3001·62	33306·0	3001·73	33304·4	−0·5
		Q_2	1·14	10·9	1·19	10·4	
8	0, 1	P_1	2988·90	33447·4	2988·82	33448·3	+1·2
		Q_1	8·33	53·8	8·29	54·2	
4†	1, 2	P_1			2973·5	33621	+2
		Q_1			—	—	
8	0, 1	P_2	2970·30	33656·8	2970·38	33655·9	+0·9
		Q_2	—	—	0·02	60·0	
3†	1, 2	P_2			2955·0	33831	+4
		Q_2			—	—	
8	0, 0	P_1	2942·30	33977·1	2942·19	33978·4	+0·3
		Q_1	1·73	83·7	1·67	84·4	
8	0, 0	P_2	2924·41	34185·0	2924·38	34185·3	−0·7
		Q_2	3·86	91·4	3·92	90·7	
8	1, 0	P_1	2883·00	34675·8	2882·92	34676·9	+0·1
		Q_1	2·37	83·6	2·37	83·5	
8	1, 0	P_2	2865·90	34882·8	2865·80	34884·1	−0·6
		Q_2	5·33	89·8	5·28	90·4	
10‡					2829·25	35334·7	
5					8·55	42·1	
7‡§	2, 0	P_1	2826·30	35371·6	2826·15	35373·4	+0·7
		Q_1	—	—	—	—	
6					2823·56	35405·9	
8‡					2812·81	35541·2	
					2·40	46·4	
10‡§	2, 0	P_2	2809·79	35579·4	2809·70	35580·5	−0·1
		Q_2	9·15	87·5	9·19	87·0	
10					2807·18	35612·5	
4					2788·27	35854·0	
4					87·01	870·2	
6					83·63	913·7	
7§	3, 0	P_1	2771·9	36065·1	2772·00	36064·4	−1·4
		Q_1	—	—	—	—	

Table 1 (*cont.*)

v', v''	Band-head	λ 2436 system, C → X				λ 2232 system, D → X			
		Int.	λ (air)	ν (vac.)	$\nu_{obs.}-\nu_{calc.}$	Int.	λ (air)	ν (vac.)	$\nu_{obs.}-\nu_{vac.}$
1, 7	P_1	00?	2625·07	38082·9	− 2·2				
0, 6	P_2	0?	23·05	112·2	− 2·6				
0, 5	P_1	1	01·51	427·7	− 1·2				
0, 5	P_2	1	2588·31	623·8	0·0				
0, 4	P_1	1	67·27	940·2	− 2·1	0	2341·13	42701·3	+0·8
1, 5	P_1	1‖	57·5	39089	−10				
0, 4	P_2	2	54·52	134·6	− 2·6				
1, 5	P_2	1	44·30	291·7	− 1·8				
0, 3	P_1	4	33·45	460·0	− 0·1	1	2313·10	43218·7	+0·5
0, 3	P_2	1	21·02	654·6	− 0·4				
0, 2	P_1	4	00·30	983·1	+ 0·8	2	2285·53	740·0	−0·4
0, 2	P_2	6	2488·21	40177·4	+ 0·2	2	74·71	948·0	−0·3
0, 1	P_1	6	67·77	510·2	+ 1·3	5	58·38	44265·8	−1·2
0, 1	P_2	7	56·03	703·8	0·0	5	47·75	475·1	+0·2
0, 0	P_1	¶	[35·91	41039·9	0·0]	4	31·53	798·3	+0·3
1, 1	P_1	2	27·68	179·1	+ 0·4				
0, 0	P_2	3	24·39	235·0	+ 0·2	4	21·24	45005·8	−0·1
1, 1	P_2	2	16·16	375·4	+ 1·8				
1, 0	P_1	6	2396·73	710·8	+ 1·1	1?	2198·9	45461	
1, 0	P_2	5	85·58	905·7	+ 1·1				
2, 0	P_1	1	59·10	42376·1	+ 1·0				
2, 0	P_2	0‖	48·6	566	− 4				

? Rather doubtful head.

* Band certainly present but head difficult to locate exactly.

† Datta's spectrogram[3] shows these heads well separated from, and on the short-λ side of, the N_2 second positive bands at λλ 2977 and 2962, but they are not marked by symbols or λ values. They are easily visible in the enlarged print from which figure 1 has been made. The heads are very difficult to locate and their assignment to the 1, 2 band is tentative.

‡ Sharp or line-like head, or strong line superposed on head.

§ Although these heads occur near the positions expected for the 2, 0 and 3, 0 band-heads, they probably do not belong to this system. All the data below the horizontal line in table 1 are for bands which may be due to a chloride of silicon other than SiCl (see p. 571).

‖ Measured only in low-dispersion spectrograms. Very rough data taken from earlier paper[2].

¶ Sub-band present but head too near to strong Si line λ 2435·159 for reliable measurement. Roughly measured in earlier low-dispersion plates[2] as λ 2436·2, ν 41035. Values of λ and ν from equation inserted here.

system, we may roughly represent the band-head wave-numbers by the following equations:

λ 2232 system, D → X,

$$\nu = \begin{Bmatrix} 44941{\cdot}5 \\ 44733{\cdot}6 \end{Bmatrix} + (663u') - (535{\cdot}4u'' - 2{\cdot}20u''^2),$$

λ 2436 system, C → X,

$$\nu = \begin{Bmatrix} 41165{\cdot}4 \\ 40970{\cdot}5 \end{Bmatrix} + (674{\cdot}2u' - 2{\cdot}20u'^2) - (535{\cdot}4u'' - 2{\cdot}20u''^2),$$

λ 2942 system, B → X,

$$\nu = \begin{Bmatrix} 34102{\cdot}7 \\ 33894{\cdot}8 \end{Bmatrix} + (701{\cdot}5u' - 1{\cdot}40u'^2) - (535{\cdot}4u'' - 2{\cdot}20u''^2),$$

where $u' = v' + \frac{1}{2}$, $u'' = v'' + \frac{1}{2}$, and the independent coefficients roughly locate the system-origins; the residuals, $\nu_{obs.} - \nu_{calc.}$, are included in table 1. The next

Table 2.** Deslandres arrangements of wave-numbers of P_1 and P_2 heads

v'	v'' → 0	1	2	3	4	5	6	7
	(D)					λ 2232 system		
1	—							
	45461 ?							
	—							
	663?							
	45005·8	44475·1	43948·0					
	207·5	209·3	208·0					
0	44798·3	44265·8	43740·0	43218·7	42701·3			(X)
		532·5 530·7	525·8 527·1	521·3	517·4			
	(C)					λ 2436 system		
	42566‖							
2	190							
	42376·1							
	660							
	665·3							
	41905·7	41375·4				39291·7		—
1	194·9	196·3				202·7		
	41710·8	41179·1				39089‖		38082·9?
	670·7	671·6				667·9		
	[670·9]	668·9				661·3		
	41235·0	40703·8	40177·4	39654·6	39134·6	38623·8	38112·2?	
0	[195·1]	193·6	194·3	194·6	194·4	196·1		
	[41039·9]¶	40510·2	39983·1	39460·0	38940·2	38427·7		(X)
		[529·7] 531·2	527·1 526·4	523·1 522·8	519·8 520·0	512·5 510·8	511·6	
	(B)					λ 2942 system		
?3	—							
	36064·4§							
	—							
	691·0							
	35580·5§‡							
?2	207·1							
	35373·4§‡							
	696·4							
	696·5							
	34884·1		33832·1†‡	33304·4	32785·3	32274·2?		
1	207·2		206·5	207·0	208·2	209·8		
	34676·9		33625·6†‡	33097·4	32577·1*	32064·4		
	698·8		703·4	695·6				
	698·5		703·3	698·3				
	34185·3	33655·9	33128·7	32608·8				
0	206·9	207·6	206·4	209·7				
↑	33978·4	33448·3	32922·3	32399·1				(X)
		530·3 529·4	526·0 527·2	523·2 519·9	520·3 519·1	512·7 511·9		

** See footnotes to table 1.

fact to be noticed in table 2 is that the interval P_2–P_1 is about the same for the B → X and D → X systems but certainly less for the C → X system, the mean values used in the derivation of the equations being 207·9 and 194·9 cm.$^{-1}$* It

* The 1923 low-dispersion measurements[2] sufficed to show the reality of this difference, the mean intervals being then estimated as 205 and 195 cm.$^{-1}$.

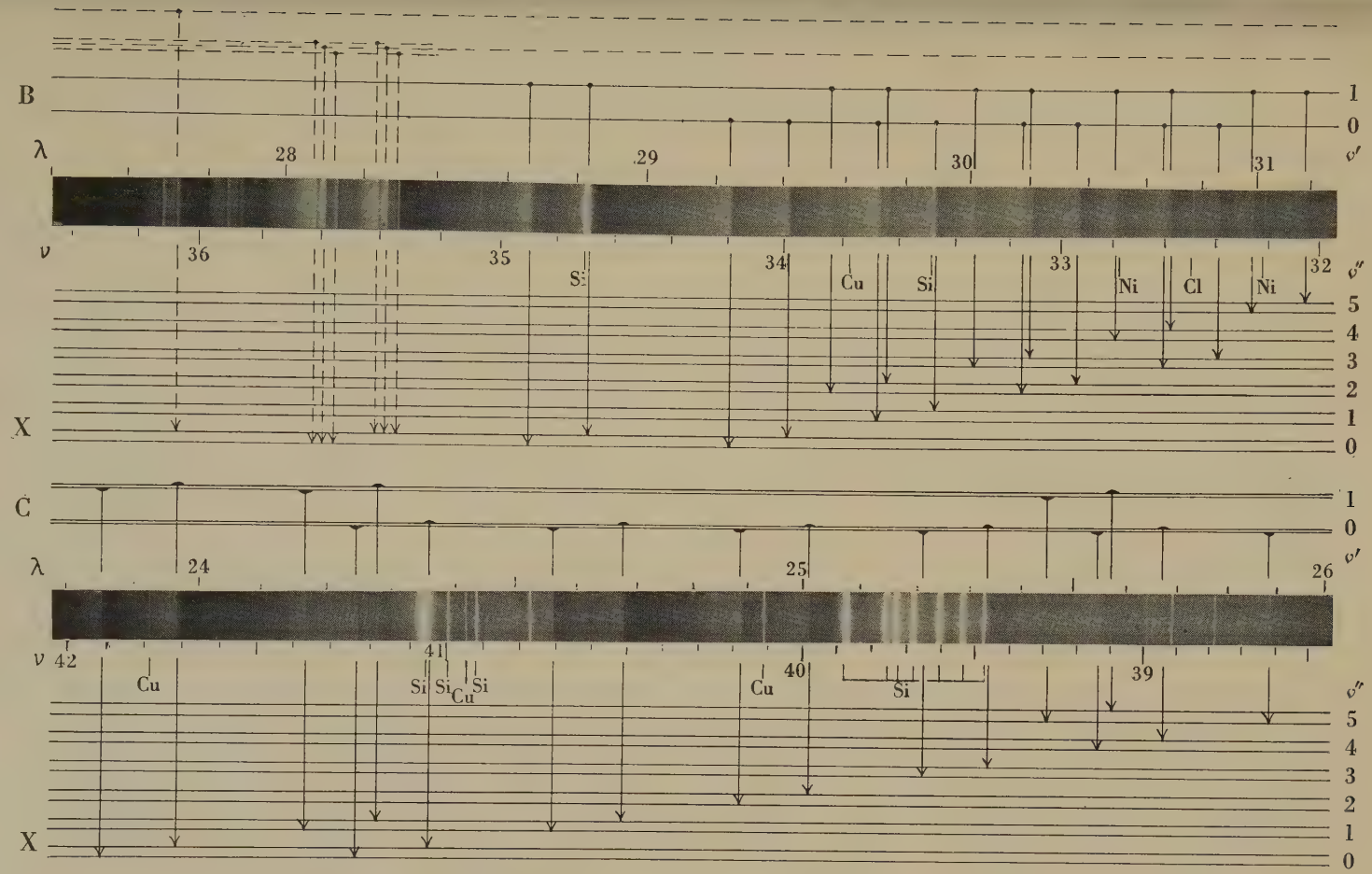

Figure 1. Two of the band-systems of SiCl and other bands (λλ 2829–2770).

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must also be noted that the sub-bands in the C → X and D → X systems are not observed to be double-headed as are those in the B → X system; in the case of D → X this may be entirely due to the use of lower dispersion; but in the case of C → X, for which the dispersion was even higher than for B → X, it seems to indicate that the bands differ in type from those of B → X.

As to the electronic separations in the states X, B, C, D, the likeliest of the three alternative assumptions possible is that made in the construction of the energy-level diagrams in figure 1 and figure 2, namely that X has the observed separation 207·9 $cm.^{-1}$, B and D are single, and the observed difference 207·9–194·9 $cm.^{-1}$ is the electronic separation in C;* in its favour is the fact that in no other way can one avoid giving the same electronic separation to two different doublet levels. With this assumption, numerical data for the four states, so far as they can be derived from the band-head measurements, may be summarized as in table 3.

Table 3. Electronic levels and vibrational constants

State	Height of $v=0$ level above that of X_1 ($cm.^{-1}$)	Vibrational constants ($cm.^{-1}$) ω_e	$\omega_{\frac{1}{2}}$	$x_e\omega_e$
D	45005·9		663 ?	
$C\ \{C_2$	41247·8	674·2	669·8	2·20
C_1	41234·8			
B	34186·0	701·5?	698·7	1·40?
$X\ \{X_2$	207·9	535·4	531·0	2·20
X_1	0			

Comparison with results of analysis of band-systems of other halides of the same sub-group affords little or no guidance to a classification of the levels X, B, C, D. Only SnCl, which emits two ultra-violet band-systems, $^2\Sigma \rightarrow {}^2\Pi$ and $^2\Delta \rightarrow {}^2\Pi$ [9,4], has electronic levels at all resembling those of SiCl. The disposition of its $^2\Pi$, $^2\Delta$ and $^2\Sigma$ is similar to that of X, C and D of SiCl, and its electronic doublets are, as they should be, wider than those of SiCl; this is shown on the right-hand side of figure 2. If these are corresponding levels in the two molecules, B may be another $^2\Sigma$; it must be noted, however, that an SnCl system corresponding to B → X has not been found although it would be expected to be strong and well situated for observation. That X, B, C, D may be $^2\Pi$, $^2\Sigma$, $^2\Delta$, $^2\Sigma$ is no more than a suggestion. Whether the first of these is the ground state of SiCl and of SnCl can only be settled satisfactorily by observations of the band-systems in absorption. A $^2\Pi$ ground state may, as Morgan [10] points out, be expected from the atomic ground states, namely $ns^2\,np^2\,{}^3P$ with $n=2, 3, 4, 5, 6$ for C, Si, Ge, Sn, Pb respectively, and $ns^2\,np^5\,{}^2P_{inv}$ with $n=2, 3, 4, 5$ for F, Cl, Br, I respectively. Unlike the emission systems of SiCl and SnCl, the single absorption system of red-degraded

* The other two, and less likely, alternatives are: (i) X single, and B, C and D double, the electronic separations being 207·9 $cm.^{-1}$ in B and D and 194·9 $cm.^{-1}$ in C. Dr Sponer [5] in tabulating Datta's results for the λ 2942 system tentatively adopts this alternative. (ii) C single, and X, B and D double, with separations 194·9 $cm.^{-1}$ in X and 13·0 $cm.^{-1}$ in B and D.

visible absorption bands* recently observed by Morgan for each of the molecules PbF, PbCl and PbBr is of a type which does not immediately suggest a $^2\Pi$ ground state, but may yet be, as Morgan says, the stronger and higher-ν sub-system of, say, a complete $^2\Sigma \rightarrow {}^2\Pi$, the undetected weaker and lower-ν sub-system being in the extreme red and near infra-red, since the $^2\Pi$ separation is expected to be of the order 7000 cm.$^{-1}$ in PbCl. For SiF Johnson and Jenkins[11] observed several band-systems, two of which were assigned to transitions to a common lower level X from levels α_1, α_2 and β respectively 22724, 22880 and 34561 cm.$^{-1}$ above it, $\alpha_1\alpha_2$ being a doublet ($\Delta\nu = 156$)[4]; since Badger and Blair[12] have recently reported that the

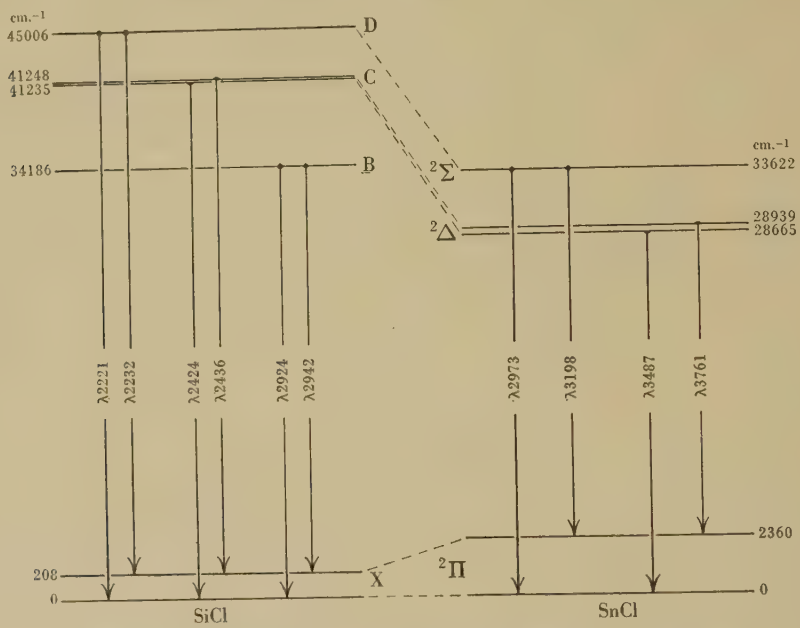

Figure 2. Electronic energy levels and band-systems of SiCl and SnCl. The widths of the double levels are exaggerated, about tenfold in SiCl and twofold in SnCl.

$\alpha_2 \rightarrow$ X bands, λ 4368, etc., are themselves double, the level X may prove to be a close doublet. For SiBr Miescher[13] has found at $\lambda\lambda$ 3233·6–2874·9 a system of emission bands whose heads are apparently single and are represented by

$$\nu = 33570 + (578{\cdot}3u' - 4{\cdot}3u'^2) - (424{\cdot}6u'' - 1{\cdot}3u''^2);$$

both of its electronic levels are single and may be $^2\Sigma$. Further observations of several halides of this sub-group, both in emission and in absorption, are much to be desired, and will, it is hoped, be undertaken as the necessary materials become available.

* *Note added March* 6: The author regrets having overlooked Rochester's recent paper[14] which records the observations and analysis of the PbF and PbCl band-systems, the former in emission and the latter in emission and absorption. It appeared simultaneously with Morgan's paper[10] and the results of the two independent investigations are in agreement. Rochester points out that Popov and Neujmin's previous analysis of PbCl fluorescence[15] is incorrect.

§ 4. OTHER BANDS

Strong bands between λ 2770 *and* λ 2830. Attention must now be directed to the bands which Datta identified as the 2,0 and 3,0 bands of the λ 2942 system. As will be seen in the plate, each sub-band of the former is the middle member of a prominent trio whose appearance is in striking contrast to that of other sub-bands in the system, their heads being very sharp or line-like and almost, if not quite, as intense as any in the system. These six heads between λ 2829·2 and λ 2807·2 occur both in the present plates of the discharge with nickel electrodes and also in the writer's 1923 plates of the discharge with aluminium electrodes and very much smaller currents; indeed, they are amongst the strong bands which, as mentioned in the opening paragraph of this paper, were measured in the first order of the 2·4-m. grating in 1923. They evidently belong to a chloride of silicon or of an impurity common to the aluminium and the nickel; their intensity suggests the former. They make up three pairs with the same, or nearly the same, separation as that already assigned to state X of SiCl, namely 207·9 $cm.^{-1}$, and would therefore appear to belong to SiCl, though not to any of the three systems described above. If this is so they require three upper levels, as indicated in broken lines in the upper left-hand corner of figure 1, with separations of about 39·0 and 32·2 $cm.^{-1}$; as the bands degrade towards the further ultra-violet these closely-spaced levels cannot, of course, be three consecutive vibrational levels of one electronic state. Against SiCl as their emitter, however, is the fact that these bands, unlike the accepted SiCl bands, show no trace of resolution into line structure. Datta makes no mention of these sub-bands, except the pair which he ascribes to the 2,0 band, although they are clearly seen in his published spectrogram[3]. The appearance of the group is, it is true, not quite the same in Datta's and the writer's plates, but this is chiefly because the former also shows with fair intensity the intervening N_2 "Second Positive" bands λ 2819·6 (3,0) and λ 2813·8 (4,1), of which there is no trace in the present plates. In the neighbourhood of Datta's 3,0 band there are, as may be seen in figure 1, also bands which do not fit into one of the above systems; unlike the former set these show some resolution into line structure. Measurements of these unallocated heads in both regions are included in the first section of table 1.

The writer is not convinced that the 2,0 and 3,0 bands of the λ 2942 system have been correctly identified, and has therefore used broken-lines for the parts of figure 1 which are in question. Without these bands the coefficients of u' and u'^2 in the equation for this system on p. 567, are not calculable; the values of ω_e and $x_e\omega_e$ for state B in table 3 are therefore queried.

Chlorine isotope effect. The abundance ratios of isotopes of Cl and Si are

$$^{35}Cl : {}^{37}Cl = 100 : 31{\cdot}4 \quad \text{and} \quad {}^{28}Si : {}^{29}Si : {}^{30}Si = 100 : 6{\cdot}95 : 4{\cdot}70,$$

and those of the only SiCl molecules that need be considered here are therefore $^{28}Si^{35}Cl : {}^{28}Si^{37}Cl : {}^{29}Si^{35}Cl = 100 : 31{\cdot}4 : 6{\cdot}95$. In the combined spectrum, then, the bands of the isotopic molecules $^{28}Si^{37}Cl$ and $^{29}Si^{35}Cl$ will have about 31 and 7 per cent, respectively, of the intensity of the corresponding bands of the main

molecule $^{28}Si^{35}Cl$. Their displacement coefficients $\rho - 1$ are not very different from one another, being $-0{\cdot}0122$ and $-0{\cdot}00967$ respectively. The band-heads of $^{28}Si^{37}Cl$ are therefore to be sought first; if they are not identified it will obviously be wrong to attribute any observed band-heads to the still rarer molecule $^{29}Si^{35}Cl$, whose bands should be only 7/31 as strong. Datta evidently overlooked this in attributing eight observed heads to $^{28}Si^{37}Cl$ and four others to $^{29}Si^{35}Cl$, the only apparent reason being that the observed displacements $\nu^i - \nu$ of these four from the corresponding main $^{28}Si^{35}Cl$ heads agreed better with the calculated displacements for $^{29}Si^{35}Cl$, $-0{\cdot}00967$ $(\nu - \nu_e)$, than with those calculated for $^{28}Si^{37}Cl$, $-0{\cdot}0122$ $(\nu - \nu_e)$. If these are real heads and are actually of isotopic origin they must all be attributed to the latter molecule.

Again, since the less abundant molecule is heavier than the more abundant, the vibrational displacements, $-0{\cdot}0122$ $(\nu - \nu_e)$, of its bands are towards the system origins ν_e throughout. And since the bands of all three systems degrade towards the far ultra-violet, the bands on the low-ν side of the system origins are not favourable to the observation of the isotopic heads, as these lie within the stronger band-structure limited by the neighbouring main heads; such bands form much the greater part of each of the SiCl systems. However, seven of Datta's twelve isotopic heads occur on this side of ν_e in the λ 2942 system. The bands where the isotopic heads are more favourably placed for observation outside the neighbouring strong band-structure are those on the high-ν side of ν_e. Of these, which, unfortunately, are very few in the SiCl systems, the 0,0 band of each system has a very small displacement, $-0{\cdot}0122$ $(\nu - \nu_e)$, and the same is true of the 1,1 band (which, moreover, is badly overrun by the 0,0 band) in the λ 2436 system; the 2,0 and 3,0 bands of the λ 2942 system are, as already stated, probably not detected; and the 1,0 band of the λ 2232 system is doubtful and very weak. The only favourable bands are therefore the 1,0 in the λ 2942 system and the 1,0 and 2,0 bands in the λ 2436 system, and it is for just these three bands, and no others, that faint and somewhat doubtful heads measured in the present plates may be assigned to $^{28}Si^{37}Cl$. Being overrun by partially resolved structure of other bands they are not easy to measure, and no great accuracy is claimed for the results, which are given in table 4.

Table 4. Cl isotope effect; observed band-heads of $^{28}Si^{37}Cl$

System	Band-head	Datta			Author			$\nu^i - \nu$ calculated
		λ^i	ν^i	$\nu^i - \nu$	λ^i	ν^i	$\nu^i - \nu$	
λ 2942	1, 0 $\{P_1$*	2883·72	34667·3	−8·5	—	—	—	− 9·5
	1, 0 P_2	2866·64	34873·8	−9·0	2866·53	34875·2	− 8·9	− 9·5
λ 2436	1, 0 $\{P_1$				2397·20	41702·6	− 8·2	− 9·0
	1, 0 P_2				2386·05	41897·5	− 8·2	− 9·0
λ 2436	2, 0 $\{P_1$				2360·06	42359·0	−17·1	−17·1
	2, 0 P_2				—	—	—	

* Datta uses the Q_1 head which gives $-16{\cdot}3$ cm.$^{-1}$ as the observed $\nu^i - \nu$. Datta's other three isotopic heads on this side of ν_e in this system are assigned to his 2,0 and 3,0 bands, which are discussed on p. 571.

§ 5. ACKNOWLEDGMENTS

The writer has pleasure in thanking the Fereday Electors of St John's College, Oxford, for the opportunity they have afforded him of carrying out further spectroscopic investigations; the Rector of the Imperial College, Prof. G. P. Thomson and Prof. H. Dingle for the excellent facilities placed at his disposal in the Astrophysics laboratories of the College; and the Government Grant Committee of the Royal Society for grants for apparatus, some of which has been used in the work recorded in this paper.

REFERENCES

(1) Jevons, W. *Proc. roy. Soc.* A, **89**, 187 (1913).
(2) Jevons, W. *Proc. roy. Soc.* A, **106**, 174 (1924).
(3) Datta, A. C. *Z. Phys.* **78**, 486 (1932).
(4) Jevons, W. *Report on Band Spectra of Diatomic Molecules*, Phys. Soc. (1932).
(5) Sponer, H. *Molekülspektren und ihre Anwendung auf chemische Probleme* (Berlin, 1935–6).
(6) Mahanti, P. C. *Z. Phys.* **88**, 550 (1933).
Bhaduri, B. N. and Fowler, A. *Proc. roy. Soc.* A, **145**, 321 (1934).
(7) Ritschl, R. *Z. Phys.* **42**, 172 (1927).
(8) Saper, P. G. *Phys. Rev.* **42**, 498 (1932).
(9) Jevons, W. *Proc. roy. Soc.* A, **110**, 365 (1926).
Ferguson, W. F. C. *Phys. Rev.* **32**, 607 (1928).
(10) Morgan, F. *Phys. Rev.* **49**, 47 (1936).
(11) Johnson, R. C. and Jenkins, H. G. *Proc. roy. Soc.* A, **116**, 327 (1927).
(12) Badger, R. M. and Blair, C. M. *Phys. Rev.* **47**, 881 (1935).
(13) Miescher, E. *Helv. Phys. Acta*, **8**, 587 (1935).
(14) Rochester, G. D. *Proc. roy. Soc.* A, **153**, 410 (1936).
(15) Popov, B. and Neujmin, H. *Phys. Z. Sowjet.* **2**, 394 (1932).

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TRANSMISSION OF LIGHT THROUGH A PILE OF PARALLEL PLATES

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ABSTRACT. The transmission of light through a pile of transparent plates is calculated by a simple method which gives incidentally the fractions of transmitted and reflected light passing at any surface in the system.

It is assumed that all the light incident upon each surface is either reflected or refracted regularly, and that the plates and the separating medium are transparent. Previous treatments of this simple case, for instance that of Baker[1], have summed the infinite series of intensities into which the light is split up. The method given below avoids this summation, and at the same time gives a simple formula for the fractions of light passing in either direction at any surface in the system. These latter results have been applied by the writer in an investigation of the photoelectric properties of transparent films, and it was in order to derive them that the method was developed.

It should be noticed first that in the region between two reflecting surfaces the rays considered together make up two beams going in opposite directions, and if we write down the reflection and transmission relations for each of these beams, then automatically we take into account the whole infinite assembly of multiply reflected rays. This underlying idea has already been used by Smith[2] in a more general treatment including scattering and absorption. Secondly, in order to discover how these beams change as we travel through successive regions between surfaces, it is simplest to consider first the end of the system farthest from the incident light, for here everything can be worked out in terms of the beam leaving the system. It is impossible to begin at the other end because, besides the incident light, there is also the unknown amount of reflected light.

n Beginning at the farthest end, let the surfaces be numbered 1 to n. Let the intensity of the light falling on the nth surface in the same direction as the light q_n, p_n incident on the system be denoted by q_n, and that in the opposite direction by p_n. The same letters can be used for both surfaces of a plate because the reflective and transmissive factors are the same for light incident in either direction on a surface. r If r is the reflection factor, the equations for the beams between two surfaces are then

$$p_{n+1}=(1-r)\,p_n+rq_n \qquad \text{.....(1)},$$

$$q_n=(1-r)\,q_{n+1}+rp_{n+1} \qquad \text{.....(2)}.$$

Adding equations (1) and (2) we get

$$q_{n+1}-p_{n+1}=q_n-p_n.$$

Therefore $$q_{n+1}-p_{n+1}=q_n-p_n=\ \dots\ =q_1-p_1=q_1,$$

since $$p_1=0.$$

Substituting for q_n in equation (1) we have

$$p_{n+1}=p_n+rq_1.$$

Therefore $$p_{n+1}=p_1+nrq_1=nrq_1,$$

and $$q_{n+1}=(1+nr)\,q_1.$$

The actual value of q_1 for a given set of plates will be proportional to the amount of light falling on the system; and as we are only concerned with the ratios of the beams, q_1 may be taken as unity. Thus

$$p_{n+1}=nr \qquad \dots\dots(3),$$

$$q_{n+1}=1+nr \qquad \dots\dots(4).$$

For a system with n surfaces, the incident light q_n must be taken as $1+(n-1)\,r$. The transmitted light will be $(1-r)\,q_1$, i.e. $(1-r)$. The fraction transmitted by a system of N plates ($2N$ surfaces) is therefore

$$\frac{1-r}{1+(2N-1)\,r},$$

and the fractions passing at any place in the system are obtained from equations (3) and (4).

The general effect of reflection on photometric measurements has also been treated by Smith in a later paper[3] in which the above expression for the transmission is derived as a special case.

REFERENCES

(1) T. Y. Baker. *Trans. Opt. Soc.* **22**, 88 (1920–1).
(2) T. Smith. *Trans. Opt. Soc.* **27**, 317 (1925–6).
(3) T. Smith. *Proc. Phys. Soc.* **44**, 314 (1932).

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WOOD-WATER RELATIONSHIPS, 2: THE FIBRE SATURATION POINT OF BEECH WOOD

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ABSTRACT. In order to determine the fibre saturation point of beech wood as accurately as possible, the vapour-pressure isothermal at high relative vapour pressures is measured on small blocks at 23° C., both for the adsorption cycle and for desorptions from three moisture-contents of 83, 47 and 120 per cent, the last value representing approximately complete saturation of the cell structure. Whereas on adsorption a vapour pressure indistinguishable from saturation appears to be reached at about 45 per cent moisture-content, which is much higher than that indicated by most routine methods, it is shown that on desorption the vapour pressure drops slightly at a moisture-content of about 90 per cent and also that the shape of the subsequent desorption curve is considerably influenced by the initial saturation moisture-content from which the drying commences. The observation made by Urquhart[13] on natural cotton, that the first desorption cycle is not reproducible once the material has been completely dried, is found to apply also in the case of beech wood. It is pointed out that there is no discontinuity in size between the botanical and colloidal capillaries and that therefore the fibre saturation point cannot be defined, except as an approximate point at which the change of moisture-content begins to produce an appreciable effect on the particular property of wood under consideration.

§ 1. INTRODUCTION

OWING to the practical importance of knowing the amount of water which wood will take up in a saturated atmosphere, a special term, the *fibre saturation point*, has come to be used for this value. It was originally defined by Tiemann[1] as the moisture-content at which further reduction causes an increase in strength of the wood, but it is now more generally described as the moisture-content at which the cell wall is saturated with water but the cell cavities empty[2] or as a value analogous to the limit of absorption of liquid by a jelly[3] which means in effect that it is the minimum moisture-content in equilibrium with a saturated atmosphere; the word "minimum" being required because wood may retain in the cell spaces large quantities of free water.

For purposes of routine measurement in this and other Forest Products Laboratories, the fibre saturation point is estimated from the moisture-content at which certain discontinuities occur in the change of the physical properties of the wood with moisture-content[2,4]. The properties usually investigated are: the maximum crushing strength parallel to the grain and the shrinkages in the radial and tangential directions. The fibre saturation point has also been determined by Stamm[3] from the change in electrical conductivity of wood.

Table I gives the average results obtained in this laboratory on a large number of specimens for six separate consignments of Beech and those quoted by Stamm for Sitka spruce.

The wide discrepancy between these values for the fibre saturation point has thrown doubt on the validity of such methods, but whatever the limitations of these indirect methods, the true fibre saturation point may be defined provisionally as the dividing line between the free and bound water in the wood, and moisture may be said to be "bound" when it exerts a vapour pressure less than saturation. The present experiments were undertaken to try to determine the true fibre saturation point in this way.

The {vapour pressure, moisture-content} isothermal (in future referred to as "*the isothermal*") has been determined for a few woods[5,6,7,8] and these show a curve similar in shape to those found for other hygroscopic materials, such as cotton[9]. They also show the usual hysteresis; that this hysteresis is of practical importance in the equilibrium moisture-content of wood in normal use has been shown by Knight in this Laboratory[10]. Since in practice the isothermal curves are drawn through a series of experimental points it is not unusual to take the

Table 1. Comparison of fibre saturation points by routine methods

Laboratory consignment number	Specific gravity*	Fibre saturation point by			
		Maximum crushing strength (per cent)	Shrinkage		Electrical conductivity
			Radial (per cent)	Tangential (per cent)	
Beech (F.P.R.L.)					
10	·562	24·9	27·1	34·1	—
23	·541	23·8	27·5	35·3	—
24	·548	23·9	26·5	34·7	—
35	·561	24·3	27·2	34·2	—
40	·580	24·0	24·3	34·0	—
46	·548	25·4	25·4	31·0	—
Sitka spruce (F.P.R.L.) 25	·356	25·0	23·6	26·1	—
(Stamm)	—	27·0	28·0	30·0	29

saturation point reached on adsorption as the starting point for the desorption curve also[7] giving thus a loop which closes at the saturation value. It was noticed, however, that if, after saturation had apparently been reached, the first desorption points were taken for very small reductions in moisture-content a disproportionately large drop in the vapour pressure occurred. This phenomenon was observed on cotton by Urquhart and Williams[9] and by Lavine and Gauger[8] for wood and lignite.

The shape of the desorption curves suggests that a lowering of the vapour pressure would be found at moisture-contents considerably higher than the adsorption saturation value, implying that the hysteresis, so far from vanishing at the saturated vapour pressure, might be considerably greater at saturation than at any other vapour pressure. On the other hand, if measurements could be made with infinite accuracy it is possible that the true saturation moisture-content on adsorption would also be found to be much higher than had generally been supposed.

* I.e. dry weight/green volume.

§ 2. APPARATUS AND METHOD

A method was, therefore, evolved by which artificially high moisture-contents could be reached by free distillation of water on to the wood. Extreme accuracy in the measurement of the moisture-content had to be sacrificed but at high vapour pressures, where the changes in moisture-content are large, this limitation is relatively unimportant. The quartz spring method of McBain and Bakr[11] is not suitable for the present work because (1) artificially high moisture-contents had to be obtained and it would be impossible to prevent an unpredictable extra extension of the spring due to condensation on the spring itself. (2) The smallest impurity of the water supply would slightly lower the maximum vapour pressure obtainable so that true saturation might never be attained and (3) at saturation the slightest variation in temperature would cause free distillation on to or off the wood and no definite end-point would be found. It was, therefore, decided in seeking the saturation moisture-content to start from moisture-contents below the expected value and, by distilling small quantities of water on to the wood, to rise to others greatly in excess of it; the resulting equilibrium vapour pressure at each step being compared with the maximum obtainable by distilling some of the water into the connecting tubes of the apparatus. The saturation value was to be taken as the point of junction of the isothermal with the saturated vapour pressure line.

It has been usefully stressed by Pidgeon[12] that the maximum width of the hysteresis loop will not be attained if adsorption takes place always from a saturated vapour pressure. This source of error is small, however, and in these experiments, where all readings are practically at saturation, it is likely to be negligible. In any case, such evidence of hysteresis as is found will be the more convincing since, on Pidgeon's argument, the method here used should lend a slight bias towards its elimination.

The apparatus shown diagrammatically in figure 1 was therefore constructed, consisting of two bottles A (only one shown) containing the wood, a bottle B containing water, a tap T_1 leading to a manometer M, another tap T_2 leading to the P_2O_5 drying tube and thence through a flexible tube to the hyvac pump. The tap T_3 served to admit air slowly through a leak L, while the bulb V (200 cm^3) gave additional volume to the manometer space. This glass work was supported on a frame which could be lowered into a water bath at $23{\cdot}00 \pm 0{\cdot}02°$ C. The bottles A were of about 10 cm^3 capacity and fitted with a cap so made that a quarter turn closed the hole H when the bottles were removed at the joint J for weighing. The bottle B was similar except that it also contained a small coil of nickel-chrome wire which, when electrically heated, caused slow evaporation of the water. To keep the tops of the bottles A dry, a diving bell D with a lead ring R as sinker was used as shown, resting on part of the frame; the bottoms of A being in the water of the bath so as to be efficiently controlled in temperature. B was completely covered by D. To open and close the bottles while in the bath, glass rods, which extended horizontally beyond the edge of D, were joined to the bottles and to the tap T_1, so that these could be turned from above with a glass hook. This was

important because if the bottles were open while being lowered into or removed from the bath, considerable migration of moisture could take place owing to temperature differences inside *D*.

The manometer *M* was of 18-mm. bore, the limbs being connected by a length of 2-mm. tubing to prevent a rush of mercury when air was admitted. The heights were read through the plate-glass side of the tank to 0·05 mm. or by judgment to 0·02 mm. on a Casella cathetometer which gave a magnified image of the meniscus. Each reading taken near saturation was compared with the saturation value obtained by closing *A* and opening *B* without otherwise altering the setting, and checked

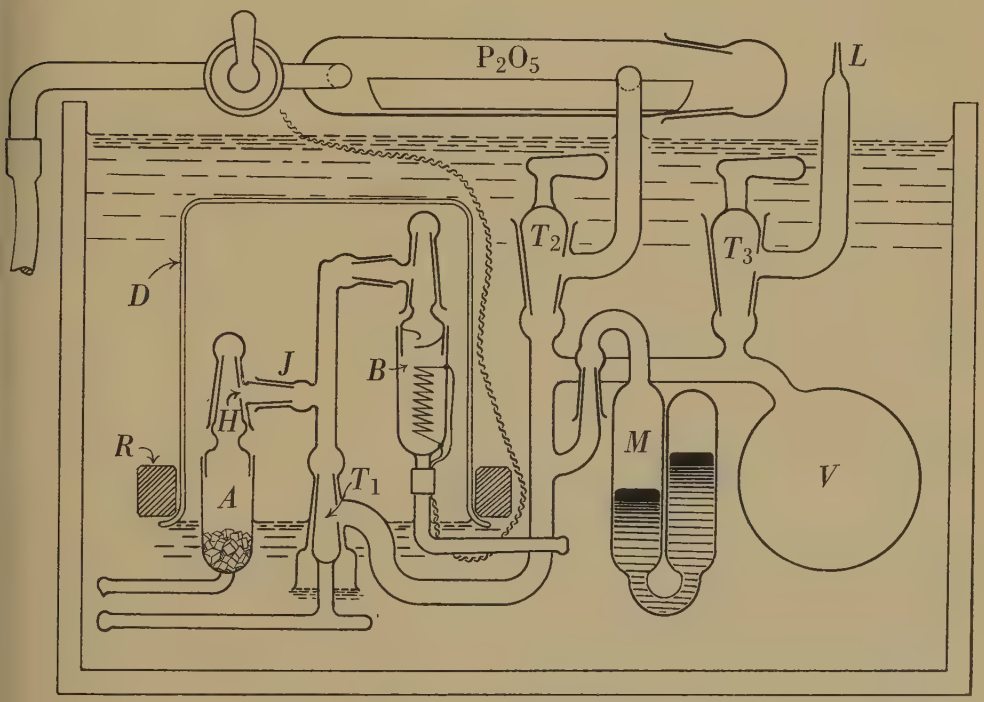

Figure 1. Diagrammatic sketch of apparatus.

against the reading obtained after a misty condensation had been obtained in the connecting tubes of the apparatus by warming *B*. A correction was also made for slight variations in temperature at the time a reading was taken. Under these experimental conditions it was considered that relative vapour pressures of 0·1 per cent or less could be detected, and of 0·25 per cent measured with reasonable accuracy.

The bulb *V* was useful in reducing pressure errors due to slight air leaks (which occasionally occurred because the bottles had to be removed for each weighing) but chiefly because, in the event of a leak, the bottles could be evacuated without loss of moisture by repetitions of a cycle involving, firstly the evacuation of the space between T_2 and *H*, then the saturation of this space with water vapour and

finally opening *H*. This method was also used for the initial evacuation of the samples and of the water in *B*.

§ 3. PROCEDURE

Approximately 0·5 g. of air-dry beech, cut into about 2-mm. cubes to ensure that all the cells were cut open at least once, was placed in each bottle *A*. These were evacuated without drying, and left all day* to reach equilibrium with the manometer. If no heat was supplied to *B*, the wood usually took up from about 35 to 40 per cent of moisture which is higher than the values given in table 1, but on being isolated from *B* the vapour pressure dropped slightly, showing that even at this moisture content the saturation value had not been reached. The next step was to condense water on to the wood. This was done outside the thermostat by warming *B*, and slightly cooling *A*, round the bottom only, with ether. In this way moisture condensed on the glass wall only where it was in contact with the wood and was subsequently absorbed by it, leaving the wall dry. It was shown that this temporary cooling had no measurable effect on the subsequent behaviour of the wood. The bottles being closed, the apparatus was now replaced in the bath for at least 1 hour before the bottles were opened to the saturated manometer space to take up equilibrium pressure. The moisture-content of the wood could thus be raised by steps to any desired value. Finally, for the desorption cycle, drying could be effected by slightly opening the tap T_2 for a few seconds to the P_2O_5 in *D*.

As will be seen from table 2 a few slight desorptions were included in the initial wetting cycle, and also one readsorption during the first drying cycle. Subsequent cycles were made continuously between the wet and dry conditions.

To avoid unwanted hysteresis effects on reassembling for further adsorption, the manometer space was always saturated before the bottles were opened, while on desorption the manometer space had to be dry. If, after weighing, the bottles were lowered into the bath while their upper parts were surrounded by cool air in *D*, moisture distilled into the cap of the bottles. To overcome this, *D* was filled with warm air before lowering into the tank. For the same reason the bottles were always handled by the cap during weighing.

Tests made on the empty bottles to determine whether condensation on the glass walls was appreciable, showed that errors from this cause could easily be avoided. The dry weight of the wood, on which all moisture-contents are based, was taken at the end of each drying cycle, by evacuating strongly over P_2O_5.

§ 4. RESULTS

The results are shown in table 2 where the desorption values are printed in italics, while figure 2 gives those for bottle 2 only. The adsorption saturation value is certainly higher than any of the values recorded in table 1, but the increased

* In general the bottles were left to set up equilibrium with the manometer for some 20 hours. A few tests were made by leaving them from 2 to 4 days but these were indistinguishable on the curve, so it may be assumed that equilibrium is established in 20 hours.

accuracy of measurement has had the paradoxical result of making the true saturation point more difficult, rather than easier, to determine because the more closely saturation is approached the more nearly does the isothermal curve lie parallel to the saturation line. Indeed, if these points are plotted to the nearest 0·5 per cent relative vapour pressure the effect of a decrease in accuracy is clearly seen because the saturation value would be judged to lie at a much lower moisture-content.

First cycle. Whereas the adsorption saturation appears to be reached at about a moisture-content of 45 per cent, the first desorption point tends to fall below saturation at a moisture-content of about 78 per cent and the line is consistently below for all subsequent readings. Thus within the degree of accuracy claimed, there appears to be a hysteresis amounting to a moisture-content of some 30 per cent at saturation. It should, however, be noted that on the first adsorption curve there is a tendency for the vapour pressure to lie on the low side of saturation up to a moisture-content of about 60 per cent, although the assumed limit of accuracy makes it possible that these points should in fact coincide with the saturation line. It might, therefore, be held that the adsorption and desorption fibre saturation points are identical and that the hysteresis loop closes at some very high moisture-content. This observation of delayed saturation is not, however, supported in the second wetting cycle where a pressure indistinguishable from saturation is reached at a moisture-content of 46 per cent. Only by extreme precision could this point be settled experimentally.

There is further evidence in these results to show when saturation is approached on adsorption. When the samples in the two bottles are adsorbing, they will do so initially at slightly different rates which will depend on chance causes, but while equilibrium is being set up they will come ultimately to the same moisture-content (except for possible slight differences due to hysteresis effects during the moisture exchange). Close to saturation, however, there will be practically no vapour pressure gradient and the moisture-contents will in general remain different. This is well shown in the last column of table 2 where for example reading No. 40 shows equal moisture-contents of 40·6 per cent, whereas for No. 41 the moisture-contents are different. On desorption, however, we are in general starting from different moisture-contents and when the vapour pressure begins to drop the tendency for the moisture-contents again to equalize will be masked because each sample will tend to follow its own isothermal and, as these may be very different in the initial stages, equalization of moisture-content will be delayed till quite low vapour pressures have been reached; see readings 17 to 23, 41 to 46 and 57 to 68.

Second and third cycles. The difference between the moisture-contents of the two samples on desorption emphasized the possible influence of the initial moisture-content on the position of the desorption curve while another possible factor is the effect of complete desiccation on the subsequent hygroscopicity, such as was noticed by Urquhart[13] on cotton taken direct from the boll which showed higher moisture-content values in this state than after the first drying cycle had been completed. The beech used here was similar to the natural cotton because it had been neither

Table 2*

No.	Relative vapour pressure (per cent)	Moisture-content (per cent)		Differences between bottles	No.	Relative vapour pressure (per cent)	Moisture-content (per cent)		Differences between bottles
		Bottle 1	Bottle 2				Bottle 1	Bottle 2	
4	100·5 (leak)	36·4	36·0	+ 0·4	36	56·0	10·0	9·4	+0·6
5	*98·8*	*34·6*	*33·7*	+ *0·9*	37	78·6	16·0	15·5	+0·5
6	99·8	36·6	36·0	+ 0·6	38	98·9	31·9	31·5	+0·4
7	99·8	36·7	35·9	+ 0·8	39	99·8	36·0	35·7	+0·3
8	Slight accidental desorption. Not measured				40	99·9	40·6	40·6	0·0
9	99·8	43·3	45·3	− 2·0	41	100·0	46·6	47·2	−1·1
10	*99·3*	*41·4*	*42·2*	− *0·8*	42	*99·8*	*43·7*	*44·3*	−*0·6*
11	—	48·9	53·8	− 4·9†	43	*99·6*	*41·1*	*41·1*	*0·0*
12	—	*44·3*	*51·4*	− *7·1*	44	*99·3*	*38·5*	*38·7*	−*0·2*
13	99·9	54·0	59·4	− 5·4	45	*99·0*	*36·0*	*36·1*	−*0·1*
14	*99·8*	*51·8*	*55·8*	− *4·0*†	46	*98·0*	*33·7*	*33·4*	+*0·3*
16	100·0	71·6	83·1	−11·5	47	*95·6*	*31·0*	*30·8*	+*0·2*
17	*99·8*	*68·3*	*78·0*	− *9·7*	48	*93·7*	*29·1*	*28·9*	+*0·2*†
18	*99·7*	*64·9*	*73·6*	− *8·7*		Dry weight taken here			
19	*99·7*	*61·4*	*69·0*	− *8·6*	53	100·0	120·2	121·8	−1·6
20	*99·5*	*58·4*	*65·1*	− *6·7*	54	*100·0*	*118·8*	*120·5*	−*1·7*
21	*99·7*	*54·7*	*59·8*	− *5·1*	57‡	*100·0*	*98·4*	*107·4*	−*9·0*
22	*99·6*	*51·6*	*54·3*	− *2·7*	62‡	*99·9*	*81·4*	*90·1*	−*8·7*
23	*99·5*	*46·6*	*46·7*	+ *0·1*	63	*99·8*	*75·9*	*84·5*	−*8·6*
24	*98·9*	*44·7*	*44·5*	+ *0·2*	64	*99·7*	*67·7*	*74·7*	−*7·0*
25	*98·5*	*43·0*	*42·3*	+ *0·7*	65	*99·6*	*57·8*	*63·3*	−*5·5*
26	*97·3*	*40·6*	*39·9*	+ *0·7*†	68	*99·1*	*42·7*	*43·7*	−*1·0*†
27	*93·9*	*35·5*	*35·0*	+ *0·5*	69	*98·5*	*40·4*	*41·0*	−*0·6*
28	*93·4*	*32·4* ?	*33·4*	− *1·0* ?	70	*95·8*	*35·2*	*35·2*	*0·0*
29	*92·3*	*33·0*	*32·6*	+ *0·4*	71	*92·7*	*30·2*	*30·9*	−*0·7*
30	99·5	41·4	41·0	+ 0·4	72	*89·5*	*25·1*	*25·9*	−*0·8*
31	99·6	41·7	41·3	+ 0·4	73	*63·2*	*13·2*	*12·9*	+*0·3*
32	*99·3*	*40·1*	*39·7*	+ *0·4*	74	*18·7*	*5·2*	*5·3*	−*0·1*
33	*96·5*	*38·3*	*38·0*	+ *0·3*		Final dry weight taken here			
34	*41·9*	*8·6*	*8·6*	*0* †					
	Dry weight taken here								

* Desorption values are printed in italics.

† Bottles regreased at these points.

‡ The missing entries here refer to desorptions which showed no drop in vapour pressure. The weights were therefore not taken.

completely dried nor resaturated since felling. If, therefore, Urquhart's observation is applicable also to wood, the effect of the initial moisture-content should be sought only after the first drying cycle is completed.

A second drying cycle was therefore taken (nos. 41 to 48) from 47 per cent and a third (nos. 53 to 72) from 120 per cent moisture-content, which represents approximately complete saturation of the botanical structure. Comparison of cycles 2 and 3 indicate that the effect of initial moisture-content is at first appreciable, but that the two curves converge as the vapour pressure is lowered; while the reduced hygroscopicity after drying is clearly shown by the fact that the moisture-contents of the third cycle are lower than those of the first although the initial moisture-

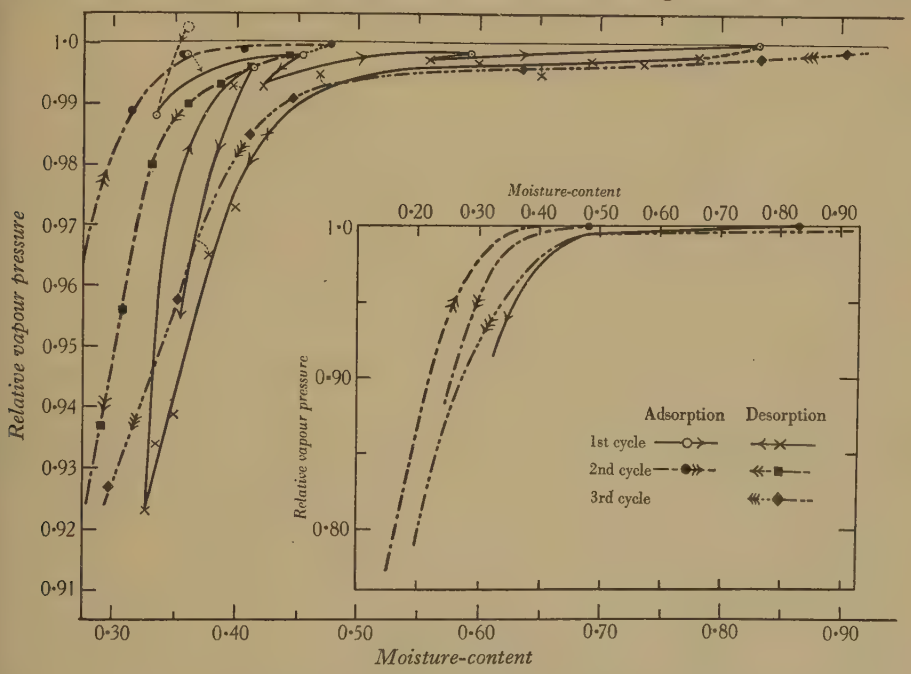

Figure 2. Vapour-pressure isothermal of small beech-wood blocks at 23° C.

content is somewhat higher. The check weighings of the dry wood taken at the end of each cycle agreed sufficiently well to show that these results are not due to experimental error, and it will be noticed by comparing the moisture-contents of the two samples at lower vapour pressures that this error does not exceed 1 per cent. The inset of figure 2 gives the outside envelopes of the three cycles in order to stress these observations.

Sitka spruce. Some measurements were also made on Sitka spruce flour at 23° C. These were done before it was fully realized that the initial moisture-content from which drying was commenced would alter the position of the desorption curve. The highest moisture-content reached was only 65 per cent, so the desorption curve shown in figure 3 must not be taken as representative of the maximum hysteresis obtainable. The values are less accurate than those for beech because the

use of flour instead of blocks added considerably to the experimental difficulties. None the less the general accuracy of the lower part of the curve (0–90 per cent relative vapour pressure) has been established by comparing it with the very accurate determination by Filby and Maass[6] at 20° C. on White spruce, which,

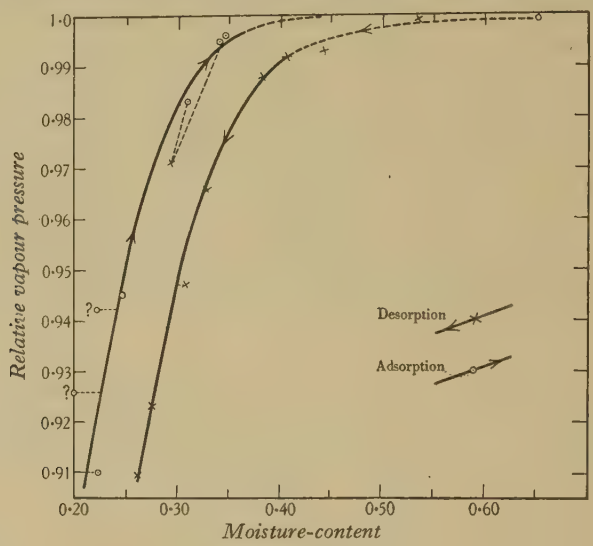

Figure 3. Vapour-pressure isothermal of Sitka spruce flour at 23° C.

though not identical in botanical structure, is closely related to Sitka spruce as far as the wood substance is concerned. The curve for White spruce lies throughout its lower range at slightly higher moisture-contents than that from which figure 3 is taken, which is to be expected from the lower temperature, and also perhaps from the intensive drying methods, employed by these workers.

§ 5. CALCULATION OF THE FIBRE SATURATION POINT FROM THE CELL-SPACE RATIO

If we adhere to the definition of the fibre saturation point as the moisture-content at which the cell spaces are empty but the cell walls are full, we can calculate the fibre saturation point, provided we know d, the specific gravity* of the wood block, ρ that of the wood substance and A the cell space ratio[14] of the block when saturated with water.

In 1 cm.³ of block there will be d/ρ cm.³ of wood substance and $(1-d/\rho)$ cm.³ of water and if m is the fibre saturation point there will be md cm.³ of water held in the cells and A cm.³ in the spaces, hence

$$md=\left(1-\frac{d}{\rho}\right)-A,$$

$d=0{\cdot}54$ may be taken as a representative value for beech and the cell-space ratio of a microsection of this specific gravity, as determined by the Wood Structure Section

* I.e. dry weight/green volume.

of this Laboratory, is approximately 0·42. Assuming that the adsorbed water retains its normal density, as is required for this calculation, ρ may be taken as very close to 1·54[15]. This gives the fibre saturation point as about 43 per cent.

§ 6. DISCUSSION

As was stated in the first paper of this series[16] it is generally agreed that, near the saturation value, at least some of the water is held by surface tension in the fine capillaries of the cell wall and that the effective radii of these capillaries may be calculated from the desorption isothermal. Now the desorption curve, figure 2, shows a drop to 99·9 per cent relative vapour pressure at a moisture-content of 90 per cent. This is very much higher than the calculated fibre saturation point given above, and indicates that it is the moisture in the cell spaces which is responsible for this drop. Fibres of beech may easily be detected whose internal radii near the ends are of the order of 10^{-4} cm. and which would, therefore, hold water at roughly 99·9 per cent relative vapour pressure. Due to local irregularities some portions of the botanical structure will have still smaller effective capillary radii so that the effect of botanical capillaries will be observable in the present experiments and may well extend to the vapour pressure of 98·6 per cent which corresponds to the calculated value of the fibre saturation point. Thus the fibre saturation point should be of significance in producing a sudden change in the physical properties of wood only if there is a discontinuity in capillary sizes at that point. This should be observable in the desorption isothermal, but since clearly no such discontinuity exists we must conclude that there is a continuous gradation of capillary sizes between the botanical and colloidal structures. The same conclusion is reached by consideration of the absorption curve which shows no definite saturation value.

The influence of a change in moisture-content on the physical properties of the wood will not, therefore, become apparent at any discrete value but only very gradually and, as all physical properties will not be equally sensitive to this influence, the wide discrepancies in the fibre saturation point indicated by different methods is at once accounted for. The reasons for these differences have already been briefly discussed[17] and will form the subject of further communications. It may also be noted that fundamental physical properties of wood, such as the heat of wetting[7] or the adsorption compression[18], also gradually approach limiting values as the moisture-content is raised and do not indicate definite saturation values.

Thus the fibre saturation point given in § 5, which cannot be calculated accurately, is of little significance from the point of view of its physical effects.

§ 7. CONCLUSION

These experiments were originally undertaken to test the validity of routine methods of determining the fibre saturation point of wood. It is obviously impossible to use exact measurements of the vapour pressure isothermal as a routine method on hundreds of individual samples of numerous species. Instead, the

methods mentioned at the beginning of the paper, are generally adopted [2,4] since the required data form part of the practical information, which it is the purpose of routine testing to supply.

Since the conclusion has here been reached that the term "fibre saturation" refers to a range of moisture-contents rather than to a discrete value, it may seem that the values of the fibre saturation point given in table 1 are of doubtful utility, but it should be borne in mind that from the point of view of working conditions each does represent the point at which a change in moisture-content begins to produce an appreciable effect on the particular property under consideration and is of great importance, provided that it is only used in relation to that property.

§ 8. ACKNOWLEDGMENTS

In conclusion I should like to thank the Director of the Laboratory, Mr W. A. Robertson for permission to publish this paper, and the Wood Structure Section for their cooperation in the measurement of the cell-space ratio.

REFERENCES

(1) Tiemann, H. D. *Bull. U.S. Div. For.* No. 70 (1906). As quoted by Hawley, L. F., *Tech. Bull. U.S. Dep. Agric.* No. 248 (1931).
(2) Wilson, T. R. C. *Tech. Bull. U.S. Dep. Agric.* No. 282 (1932).
(3) Stamm, A. J. *Industr. Engng Chem.* **1**, 94–7 (1929).
(4) E.g., *Bull. For. Prod. Res.*, Lond., No. 10 (1931).
(5) Pidgeon, L. M. and Maass, O. *J. Amer. chem. Soc.* **52**, 1053 (1930).
(6) Filby, E. and Maass, O. *Canad. J. Res.* **7**, 1 (1935).
(7) Stamm, A. J. and Loughborough, W. K. *J. phys. Chem.* **39**, 121 (1935).
(8) Lavine, I. and Gauger, W. J. *Industr. Engng Chem.* **22**, 1231 (1930).
(9) Urquhart, A. R. and Williams, A. M. *Shirley Inst. Mem.* **3**, 197 (1924).
(10) Knight, R. A. G. *Engineering* (May 3, 1935).
(11) McBain, J. W. and Bakr, A. M. *J. Amer. chem. Soc.* **48**, 693 (1926).
(12) Pidgeon, L. M. *Canad. J. Res.* **6**, 713 (1934).
(13) Urquhart, A. R. *Shirley Inst. Mem.* **8**, 29 (1929).
(14) Barkas, W. W. *Proc. phys. Soc.* **46**, 545–58 (1934).
(15) Stamm, A. J. *J. phys. Chem.* **3**, 398–414 (1929).
(16) Barkas, W. W. *Proc. phys. Soc.* **48**, 1–17 (1936).
(17) Barkas, W. W. *Nature*, Lond., **135**, 545 (1935).
(18) Stamm, A. J. and Seborg, R. M. *J. phys. Chem.* **39**, 133–42 (1935).

DISCUSSION

Dr D. T. Davies. I have discussed this paper with Mr Barkas previously and I make this contribution largely at his request because somewhat similar work is being carried out on coal and there are certain points of interesting similarity and divergence. In the screening, dedusting and dry-cleaning of coal, freedom of movement of separate particles is essential, and many processes fail entirely if surface moisture is present.

The terms "inherent" and "surface moisture" are very loosely used in the coal industry. The former should, of course, be defined at a definite relative humidity, and account should be taken of the hysteresis effect which exists in coal as in other materials of gel structure. The figures quoted for inherent moisture probably approximate to the values that would be obtained in equilibrium at a relative humidity between 50 and 60 per cent, and they vary from about 1 to 10 per cent according to the nature of the coal. Manufacturers of dry-cleaning plant usually expect to encounter difficulties if more than 2 per cent of moisture in excess of the inherent moisture is present in the coal, but it is hardly possible that such a fixed figure should really apply to all coals.

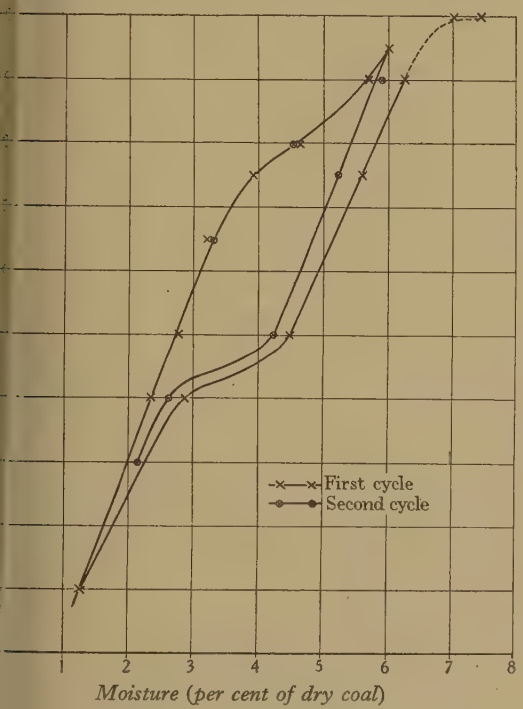

Figure 1. Isothermal of Meltonfield coal at 25° C.

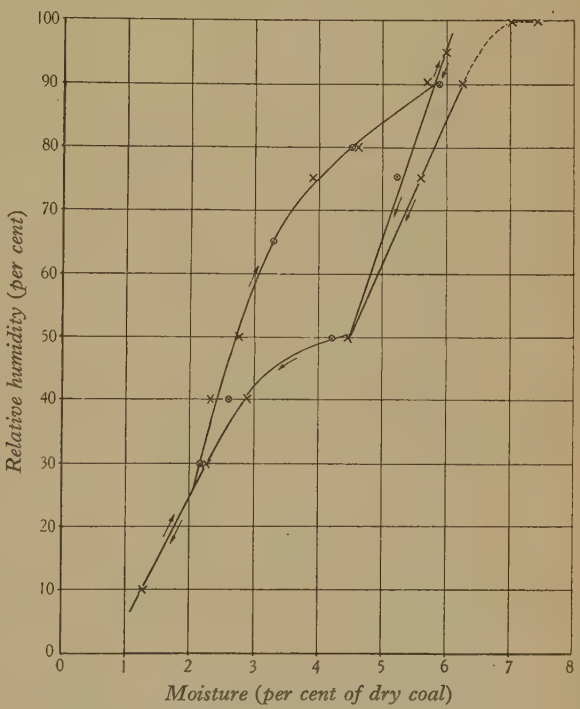

Figure 2. Isothermal of Meltonfield coal at 25° C.

A study of the mechanics of moisture-retention is being made by the Fuel Research Organization, and figure 1 shows a typical vapour-pressure isothermal produced by Dr Slater of the South Yorkshire Survey Laboratory by drawing a smooth curve through the equilibrium points. The irreversible part of the isothermal on the extreme right of the diagram was obtained by taking sample drillings from a shot-hole bored in the actual coal face below ground. It will be noted that the moisture-content of the freshly mined coal was nearly 7·5 per cent whereas in equilibrium at a relative humidity of 95 per cent the moisture-content is only 6 per cent.

In figure 2 I have taken the liberty of drawing a slightly different curve through the same points with a view to stressing the possibility of a correspondence between

the isothermals for coal and silica gel. The most important part of the curve for our purposes is the range over relative humidities of about 90 per cent, and although the data regarding this range are not nearly so complete as those put forward for wood by Mr Barkas, I have made certain observations regarding them which may be of interest.

The hysteresis loop appears to be definitely closed at a relative humidity of about 90 per cent and the range above that appears to be reversible and to correspond to true surface moisture. The point at which freedom of relative movement of particles occurs in a mass of drying coal has been termed the "dusty point" and occurs at the moisture-content corresponding to a relative humidity of about 95 per cent. In addition to these laboratory experiments it has been observed that if dry small coal is exposed to the ordinary temperatures and humidities but protected from direct access of rain, it can pick up so much moisture that it loses its dustiness. All the evidence thus appears to indicate the appearance of true external surface moisture in equilibrium at relative humidities below 100 per cent and in sufficient quantities to influence the mechanical properties of the coal.

Author's reply. The observations of Dr Davies are of interest in supporting my view that the shape of the isothermal for wood near saturation is largely determined by the size-distribution of the botanical capillaries. I understand that in coal the botanical capillaries are not empty as in wood, so that the isothermal near saturation will be determined by the colloidal capillaries and by surface sorption. Since these capillaries are small, the hysteresis effect, if due to delayed wetting of the wall on adsorption, will persist only up to a vapour pressure corresponding to the radius of curvature of the meniscus in the largest capillaries present. Owing to delayed wetting this radius will be somewhat larger than that of the capillary itself, but one may conclude that there are no capillaries larger than this in the colloidal structure of the coal. If the Thomson equation is valid, Dr Davies's figure of 90 per cent relative vapour pressure corresponds to a radius of curvature of approximately 10^{-6} cm.

While it may be true that, in the reversible portion of the isothermal, sorption on the external surface will predominate, it must be remembered that the concave menisci mentioned above will also sorb moisture at relative vapour pressures above 90 per cent until at saturation the menisci will be plane. Thus the total sorption of 6 per cent moisture-content at saturation will be the sum of the surface and capillary sorptions. The capillary sorption between a relative vapour pressure of 90 per cent and saturation will be reversible, for within this range the meniscus is always in contact with the lip of the capillary and there is no effect of delayed wetting.

621.383.2

TIME LAG IN PHOTOELECTRIC CELLS

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AND

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ABSTRACT. § 1. This work continues that of Campbell and Stoodley[1] and of Campbell[2]. § 2. Frequency-response curves are compared with oscillograph traces of the current through the cell when light is suddenly thrown on or off it. A theory of the comparison is given; it is shown that the comparison provides a test of the "assumption of independence", i.e. the assumption that time lag arises wholly in processes following a single instantaneous light-impulse, and not from the interaction of succeeding impulses. The experiments are wholly adverse to the assumption; low-frequency time lag must arise in great part from such interaction. The evidence on which the assumption was based previously is re-examined; it is found to be exceptional and not typical, and therefore quite inconclusive. § 3. Attempts to determine directly how time lag is affected by the size of the cells, other things being as far as possible equal, failed because it was evident that factors other than those contemplated were being varied accidentally. But measurements on a single long cell with several anodes indicated that low-frequency time lag is not due directly to the finite velocity of the ions. Incidentally the positive ion current was found—as is to be expected—to show greater time lag than the whole current. § 4. The experiments on cells cooled in liquid air, described in paper II, were continued; the previous results were confirmed; temperature has an effect separate from that on the density of the gas. § 5. The very small time lag of argon-filled cells with sensitized potassium cathodes was found to be due to hydrogen evolved from the cathode. When this is removed the time lag increases greatly. Further investigation of this remarkable result is deferred. § 6. In a brief discussion it is pointed out that the distinction previously made between low-frequency and high-frequency time lag must be maintained; the latter is undoubtedly due to the finite velocity of the ions, the former is not. For the low-frequency lag metastable states are still the most plausible explanation; but there are difficulties in the failure of the assumption of independence and in the effect of hydrogen. No alternative theory is proposed at present; more facts are required.

§ 1. INTRODUCTION

THIS paper describes a continuation of the work of Campbell and Stoodley[1], and of Campbell[2]. These two papers will be referred to as *paper I* and *paper II* respectively. The new work will be described first with reference to these two papers only; its relation to the work of others will be discussed later.

* Mr Stoodley is a past, not a present member of the Staff.

§ 2. GENERAL THEORY

Calculation. The theory underlying much of paper II may be stated thus. If
L_0 light of intensity L_0 falls on the cathode only for an infinitesimal period $d\tau$ at time
τ, q $\tau = 0$, then the charge q that has crossed the cell up to time τ is given by

k $$q = kL_0 \, d\tau . f(\tau) \qquad \ldots\ldots(1),$$

$f(\tau)$ where $f(\tau)$ increases very rapidly at $\tau = 0$, and is equal to 1 for all values of τ greater
T than some limit T, which may be identified with the time lag.

So far the theory is hardly dubitable. But if it is to be of any service in explaining the effects of time lag, and in particular the form of the frequency-response curve, a further assumption must be made. It is that the effects of successive light-impulses are independent, and that if the light L incident on the cell is varying continuously, so that

$$L = L_0 \phi(t) \qquad \ldots\ldots(2),$$

then the charge that has passed up to any given moment (from which the current can be obtained by differentiation) can be calculated by adding the effects, given by equation (1), of all the infinitesimal impulses into which the continuously varying light can be resolved. This assumption appears to have been made by most of those who have attempted to relate the form of the frequency-response curve to the physical processes that are assumed to give rise to the time lag. Nevertheless it is by no means necessarily true; it may well be that the ions produced by earlier impulses affect materially (e.g. by the development of space charges), the number of ions produced by later impulses and the time that they take to reach the electrodes.

In paper II an attempt was made to decide the matter by direct determination of $f(\tau)$ in equation (1) and the comparison of the frequency-response curves calculated from $f(\tau)$ so determined, by the aid of the assumption of independence, with experimental frequency response curves. But the direct determination is very difficult. The first part of the work described here aimed at an indirect determination of $f(\tau)$. The indirect determination involves the assumption of independence; nevertheless it appeared that the method, though it could not establish the truth of the assumption certainly, might produce conclusive evidence of its falsity, if it is indeed false.

The theory of the method is as follows: Suppose there is thrown on the cell light varying according to the thin line in figure 1; light is thrown on the cell suddenly at $t = 0$, maintained constant for a time T so long that $f(T) = 1$, cut off suddenly, kept off for time T and so on. Then, as is known from paper I, the current
i i through the cell will vary according to the thick line. (Of course the ordinates for the thin and thick lines are different; the maximum in each case is made equal to 1.) Then, if the assumption of independence is true, it can be proved that the equation of the part of the thick line, starting from $t = 0$, is

$$i/kL_0 = f(t) \qquad \ldots\ldots(3),$$

t_1 and the equation starting from $t = T$, putting $t_1 = t - T$ is

$$i/kL_0 = 1 - f(t_1) = (\text{say}) \, f_1(t) \qquad \ldots\ldots(3').$$

The ascending and descending curves should be superposable, and each should give $f(\tau)$ directly.

Before equations (3) and (3′) are proved, it should be noted that it is impossible to turn the light on and off with perfect suddenness; the light will really vary as shown by the dotted line, taking a time θ to rise and fall. It is therefore well to take this complication into account from the start.

Equations (3) and (4) of paper II, on which calculations were based previously, are incorrect; accordingly the theory will be set forth entirely anew.*

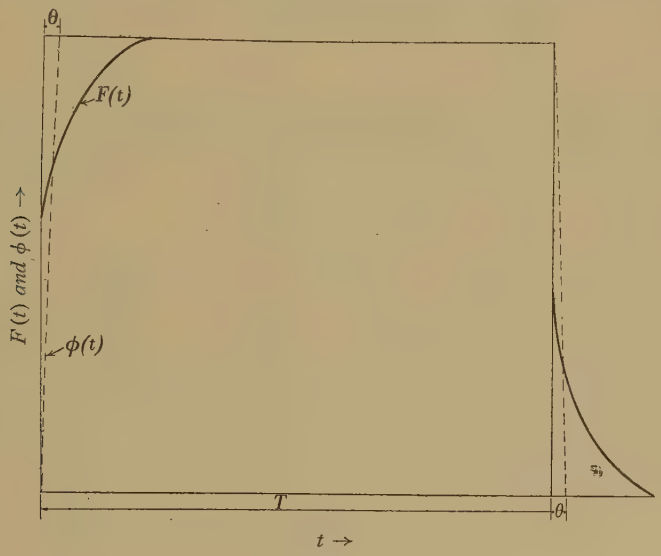

Figure 1.

If L is given by equation (2), the charge given to the electrode by a light impulse, lasting a time $d\tau$ and occurring at an interval τ before the instant of observing t, is, in virtue of equation (1),

$$q = kL_0\,\phi\,(t-\tau)\,f\,(\tau)\,d\tau \qquad \text{.....(4).}$$

The whole charge Q that has been communicated since the start of the experiment at time t_0 is, in virtue of the assumption of independence, given by

$$Q = kL_0 \int_0^{t-t_0} \phi\,(t-\tau)\,f\,(\tau)\,d\tau \qquad \text{.....(5).}$$

The current at time t is given by

$$i = dQ/dt \qquad \text{.....(6).}$$

Consequently

$$i/kL_0 = \frac{d}{dt}\int_0^{t-t_0} \phi\,(t-\tau)\,f\,(\tau)\,d\tau \qquad \text{.....(7).}$$

The experiment assumes that T is so long that the *current* at t is not affected by events before $t-T$. Hence in equation (7), but not in equation (5), we can change

* More conventional, and perhaps more stringent, proofs can be based on the accepted formulae of electric circuit theory. We prefer to start from the ultimate facts in this example.

the upper limit of integration to T; the limits are then independent of t and the differentiation can be performed within the integral. Hence

$$i/kL_0 = \int_0^T \phi'(t-\tau) f(\tau)\, d\tau \qquad \text{.....(8),}$$

θ $\phi'(t-\tau)$ is zero, except when $t-\tau$ lies between 0 and θ. If we confine our attention to values of $t > \theta$, $\phi(t-\tau)$ changes from 0 to 1, while τ changes from $t-\theta$ to t. In the limit when $\theta = 0$, $f(\tau)$ is constant and equal to $f(t)$ during this change. So that

$$i/kL_0 = f(t) \int_{t-\theta}^{t} \phi'(t-\tau)\, d\tau = f(t) \qquad \text{.....(9).}$$

This is equation (3).

If θ is appreciable, we may assume with sufficient accuracy that the rise and fall of ϕ is linear, so that $\phi'(t-\theta) = 1/\theta$ when it is not zero. Then

$$i/kL_0 = \frac{1}{\theta} \int_{t-\theta}^{t} f(\tau)\, d\tau \qquad \text{.....(10).}$$

$F(t)$ We shall call this function $F(t)$; it gives the form of the thick curve in figure 1 when θ is finite; it is given only for $t > \theta$.

The problem that we are considering is that of finding $f(\tau)$ when $F(t)$ is given from the cathode-ray trace. If the form of $f(\tau)$ is known analytically, but not the value of its parameters, the right-hand side can be integrated and a set of parameters sought that will give the required $F(t)$ for $t > \theta$. Thus, it is known that $f(\tau)$ is approximately of the form

a, λ $$f(\tau) = 1 - ae^{-\lambda\tau} \quad (\tau > 0) \qquad \text{.....(11).}$$

a' This gives $$F(t) = 1 - a'e^{-\lambda t} \qquad \text{.....(12),}$$

where $$a' = a\frac{e^{\lambda\theta} - 1}{\lambda\theta} \sim a\left(1 + \frac{\lambda\theta}{2}\right) \qquad \text{.....(13).}$$

$F(t)$ then differs from $f(t)$ only in the substitution of a' for a. If we find λ and a' from the given $F(t)$, a can be found from equation (13) if θ is known, and thus $f(t)$ determined. The frequency response curve can then be calculated and compared with the experimental curve.

If the form of $f(\tau)$ is not known and $F(t)$ is given graphically, but not analytically, $f(\tau)$ in equation (10) can be expanded by Taylor's theorem, leading to

$$F(t) = f(t-\theta) + \frac{\theta}{2} f'(t-\theta) + \ldots, \quad t > \theta \qquad \text{.....(14),}$$

which can be solved for $f(t)$ by graphical approximation. It should be observed that, in this process, we obtain only $f(\tau)$ for $\tau > \theta$; since there may be a discontinuity at $\tau = 0$, extrapolation to zero is precarious. But any reasonable extrapolation will lead to the same frequency response curves from frequencies much less than $1/\theta$.

All this applies only if $\theta < t < T$. The corresponding treatment when $T + \theta < t < 2T$ is so similar that it need not be given. It follows quite generally

that, so long as the fall of $\phi(t)$ at $t=T$ is similar to the rise at $t=0$ and occupies the same time θ, then, if F_1 corresponds to F as f_1 to f in equation (3′) F_1, f_1

$$F_1(t_1) = 1 - F(t) \qquad \text{.....(15).}$$

The rise and fall of the thick line in figure 1 should be superposable.

It remains to consider how the frequency response curve is to be calculated from $f(\tau)$ derived in this way. This curve is a relation between $i_a/\bar{\imath}$ and n, the n frequency of the light varied sinusoidally, so that equation (2) becomes

$$L = L_0(1 + e^{j\omega t}), \quad \omega = 2\pi n \qquad \text{.....(16),} \quad \omega$$

where i_a is the amplitude of the alternating component of the current through the i_a cell, $\bar{\imath}$ the main current. $\bar{\imath}$

We start again from equation (7), and now divide the range 0 to $t-t_0$ into two ranges: (1) 0 to m/n, where m is an integer so great that $f(m/n)=1$ (that is to say, m, n a large number m of complete periods extending backwards from t) and (2) m/n to $t-t_0$. For range (1) the limits of integration are independent of t, and we can differentiate within the integral; for range (2) $f(\tau)=1$. Consequently

$$i/kL_0 = \left| \frac{d}{dt} \int_{m/n}^{t-t_0} (1 + e^{j\omega(t-\tau)})\, d\tau + \int_0^{m/n} j\omega . e^{j\omega(t-\tau)} f(\tau)\, d\tau \right| \qquad \text{.....(17).}$$

Remembering that $e^{-j\omega m/n} = 1$, we have

$$i/kL_0 = \left| 1 + e^{j\omega t} + e^{j\omega t} . j\omega \int_0^{m/n} e^{-j\omega\tau} f(\tau)\, d\tau \right| \qquad \text{.....(18),}$$

$$\bar{\imath}/kL_0 = 1; \quad i_a/kL_0 = \left| 1 + j\omega \int_0^{m/n} e^{-j\omega\tau} f(\tau)\, d\tau \right| \qquad \text{.....(19).}$$

Hence, trigonometrical functions being introduced,

$$i_a/\bar{\imath} = \{(1+A)^2 + B^2\}^{\frac{1}{2}} \qquad \text{.....(20),}$$

where

$$\left.\begin{aligned} A &= \omega \int_0^{2\pi m/\omega} \sin \omega t\, f(\tau)\, d\tau \\ B &= \omega \int_0^{2\pi m/\omega} \cos \omega t\, f(\tau)\, d\tau \end{aligned}\right\} \qquad \text{.....(21).} \qquad \begin{matrix} A \\ B \end{matrix}$$

A and B can be determined by graphical integration, when $f(\tau)$ is given graphically; since $f(\tau)$ increases with τ, both A and B are always negative.

In the special case* when $f(\tau)$ has the form (11),

$$i_a/\bar{\imath} = \left\{ \frac{1 + (1-a)^2 y^2}{1 + y^2} \right\}^{\frac{1}{2}}, \quad y = \omega/\lambda \qquad \text{.....(22).}$$

Experiments. Frequency-response curves were taken as described in paper II. It is to be noted that the variation of the light was not strictly sinusoidal; but a very superficial inquiry suffices to show that the results described below are not affected by this slight departure from ideal conditions. The input resistance to the first valve of the amplifier was also so small that the capacity of the cell might be

* Equation (7) of paper II is identical with equation (22), if a misprint is corrected, and $a\omega^2\lambda^2$ replaced by $a^2\omega^2\lambda^2$. Accordingly, though equations (3) and (4) of paper II are incorrect, they lead to the right result.

taken as zero. The slight variation of amplification with frequency was ascertained by measuring the response of a vacuum cell without time lag and allowed for.

The cathode-ray oscillograph was of standard design and requires no special description. Here again a small input resistance was used. The interruption of the light, giving $\phi(t)$ the form of the dotted curve in figure 1, was effected by a rotating disc, whose edge was recessed over half its circumference. The boundary between the recessed and non-recessed half was radial; the width of the beam interrupted was such that $\theta = 1/20{,}000$ sec. The disc was rotated at 50 revolutions per second by a synchronous motor so that (in figure 1) $T = 1/100$ sec. The supply to the motor provided the time-base. The image on the screen was traced on tracing paper; it was enlarged and transferred to squared paper by optical projection.

The time $t = 0$ could always be identified by a sharp corner in the trace, but the location of the exact point was one of the main sources of error. Another source was an inclination of the flat part of the trace to the horizontal, due doubtless to the usual change of the sensitivity of the cell when current is drawn from it. The possible error arising in these and other ways is indicated in the figures below by the breadth of the curves.

The cells examined were almost all cathode-on-the wall cells, the cathode being Ag-O-Cs; the filling was usually argon, but sometimes helium. The shapes and the pressure of the argon were various; though these features affected the form of the frequency-response curves greatly, they did not seem to affect in any simple manner the relation between this curve and the cathode-ray trace. Accordingly details need not always be given. Measurements were usually made at several values of the gas factor m and the mean current $\bar{\imath}$; of course, the time lag always increased with m and, to a lesser degree, with $\bar{\imath}$. Most of the facts detailed below refer to $m = 10$ and $\bar{\imath} =$ about $2\,\mu$A.; but again precise details in every case are unnecessary.

Results. There was a general qualitative correlation of the kind to be expected, between time lag indicated by the frequency-response curve and time lag indicated by the cathode-ray trace; that is to say, the more rapidly $i_a/\bar{\imath}$ decreased with increase of frequency, the more slowly did $F(t)$ approach 1. If m or $\bar{\imath}$ were varied in a single cell, the correlation appeared to be perfect. But in the comparison of different cells, apparent departures from correlation were obvious at once; very similar cathode-ray traces sometimes corresponded to very different frequency-response curves, especially when the gas filling was different.

Further it was found that the rise and the fall of the cathode-ray trace were not superposable, as they should be according to equation (14); the difference was sometimes small; sometimes the rise was steeper, sometimes the fall. Examples of a small and a large difference of opposite signs are given in figures 2 and 3; here the curve marked Rise is $F(t)$ for $\theta < t < T$; the curve marked Fall is $F_1(t_1)$ for $\theta < t_1 < T$.

The first of these observations suggested, the second proved, that the theory expressed in equations (1) to (22) is not accurately true; for similarity of rise and fall is an inevitable consequence of the assumption of independence. Nevertheless an attempt was made to apply the results of that theory quantitatively. For this

purpose the following procedure was adopted. Examples were selected in which $F(t)$ approached the form (12) and $i_a/\bar{i}$ approached the form (22). A family of

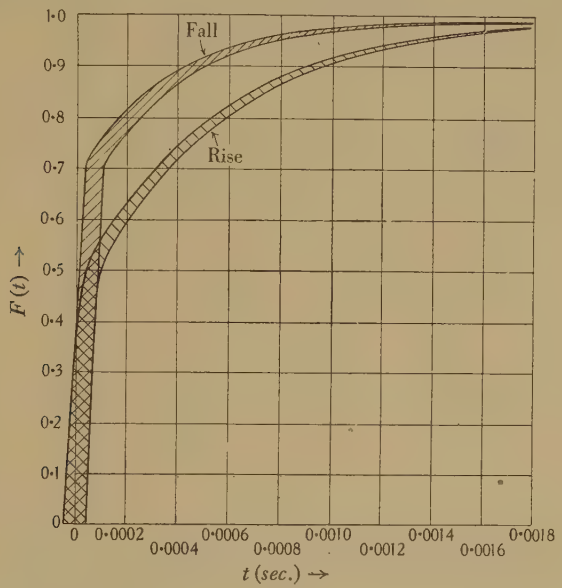

Figure 2. Rise and fall curves for small spherical cell argon filling: $m = 10$.

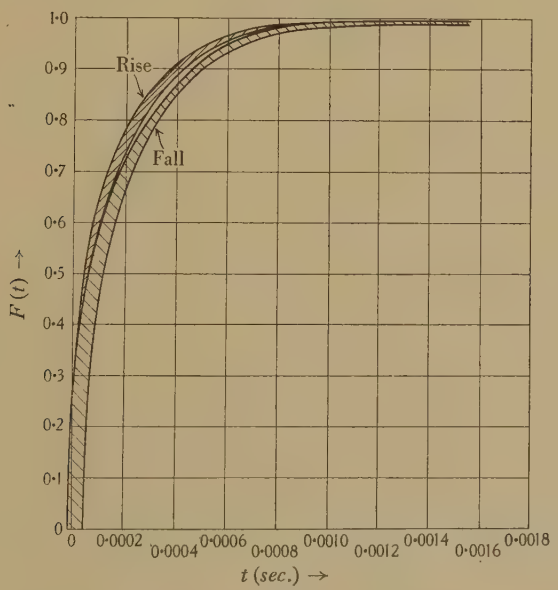

Figure 3. Rise and fall curves CMG 1.

curves $z = 1 - a'e^{-\lambda t}$ for various values of a' were plotted with $\log \lambda t$ as base; the full curves in figures 4, 6 and 8 are members of this family, the scale of abscissae being that at the top. $F(t)$, taken from the mean of the rise and fall curves, was now plotted against $\log t$. This curve was placed over the family, with the lines $z = 1$

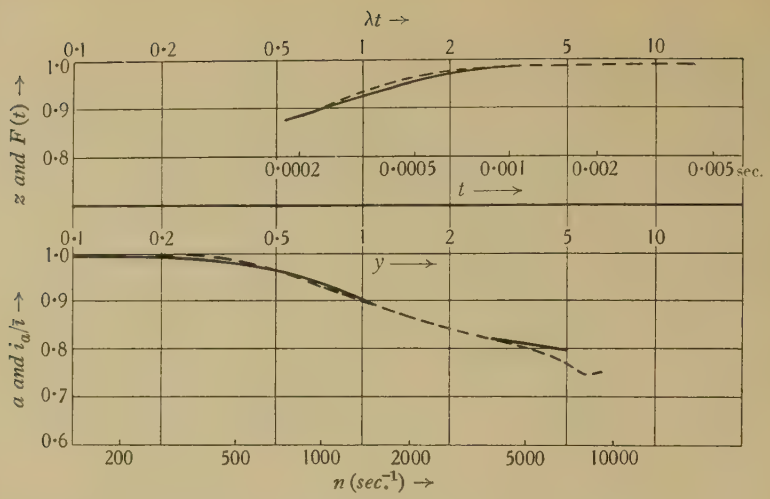

Figure 4. z against λt and $F(t)$ against t when $a'=0{\cdot}2$, $a=0{\cdot}18_5$, $\lambda=3250$.

Figure 5. a against y and $i_a/\bar{\imath}$ against n when $a=0{\cdot}2$, $\lambda=8490$.

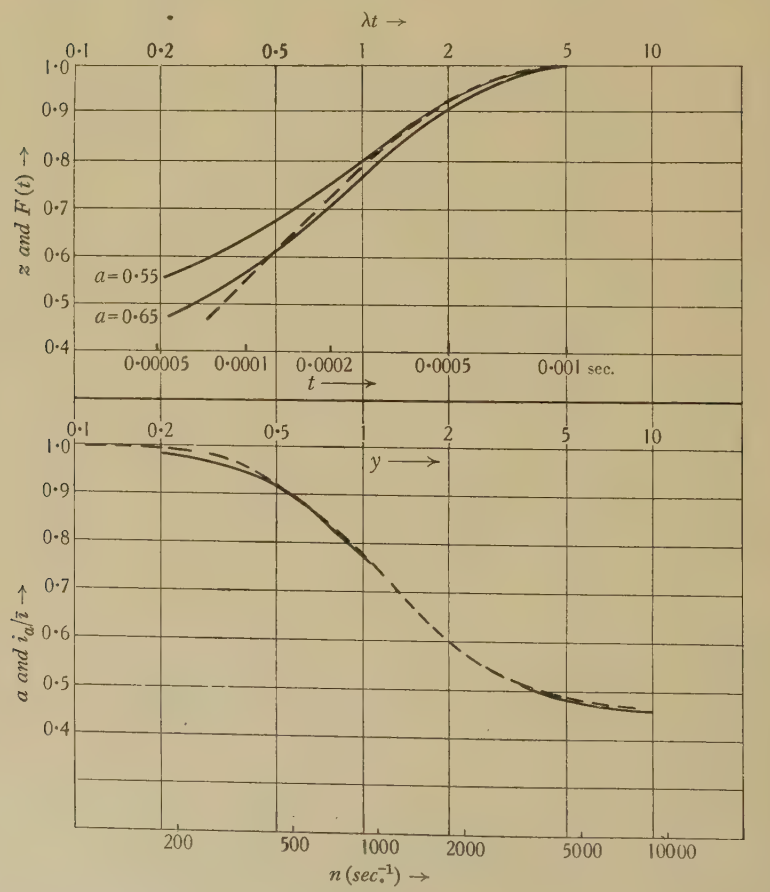

Figure 6. z against λt and $F(t)$ against t when $a'=0{\cdot}6$, $\lambda=3970$, $a=0{\cdot}55$.

Figure 7. a against y and $i_a/\bar{\imath}$ against n when $a=0{\cdot}55$, $\lambda=5500$.

and $F(t)=1$ coincident, and moved parallel to this line until the best fit between $F(t)$ and one of the family was obtained; the result is indicated by the dotted curve (where distinct from the full curve), t being shown on the lower scale. If t' is now the value on the lower scale corresponding to $\lambda t=1$ on the upper scale, the appropriate value of λ is $1/t'$; the appropriate value of a' is that for the member of the family with which the dotted curve most nearly coincides. The values of a' and λ thus deduced are shown on the figures, together with a deduced from equation (13).

A similar procedure was adopted for $i_a/\bar{\imath}$. A family of curves (22) for different values of a were plotted against log y; members of this family are given by the full

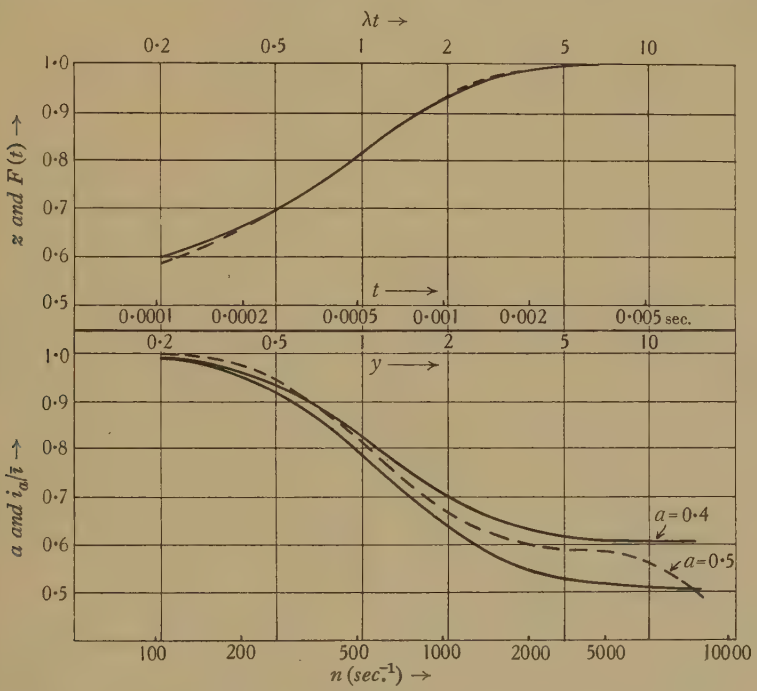

Figure 8. z against λt and $F(t)$ against t when $a'=0{\cdot}5$, $\lambda=1940$, $a=0{\cdot}475$.
Figure 9. a against y and $i_a/\bar{\imath}$ against n when $a=0{\cdot}42$, $\lambda=3270$.

lines in figures 5, 7 and 9, which correspond respectively to figures 4, 6 and 8. The frequency-response curve, plotted against log n, was brought into the best coincidence, as indicated by the dotted curve. If n' is the value on the lower scale corresponding to $y=1$ on the upper, then the appropriate value of λ is $2\pi n'$; a is given as before by the member of the family which fits.

We have thus two pairs of values (a, λ) which should coincide if the theory is true. It will be seen that, though there is some agreement in the as, λ deduced from $i_a/\bar{\imath}$ is always much greater than λ deduced from $F(t)$. The discrepancy is far beyond any experimental error; graphical integration, based on equations (14) and (20), showed that it could not be explained by the fact that $f(\tau)$ is not accurately of the form (10). The experiments prove definitely that the theory of equations (1) to (22) does not apply, and hence that the only dubitable assumption, namely that of independence, is not true.

It may be observed that this conclusion is supported even by the agreement found, namely that between the as $1-a$ is a measure of the fraction of the current that is substantially free from time lag; the agreement of the as indicates that this fraction can be deduced approximately both from $F(t)$ and $i_a/\bar{\imath}$. If $(1-a)$ turned out to be the fraction carried by the primary current, namely $1/m$, the explanation would be obvious; but actually $(1-a)$ is always much greater than $1/m$; for $m=10$ in all these examples. It appears then that there is a part of the current carried by ions or secondary electrons, and not by the primary electrons, which has no time lag, or at least a time lag less than 1/10,000 sec. (see § 6 below) and another part carried by the same agencies having a time lag greater than 1/1000 sec. The only explanation appears to be that, while the ions first produced by the primaries reach the electrodes practically instantaneously, they leave behind them some effect (e.g. space charges, polarizations, or metastable atoms) which cause the ions produced later to be subject to time lag.

We conclude then that the fundamental assumption of our theory is false, and that the effects of succeeding light impulses are not independent; time lag must arise, at least in part, from the interaction of the products of primary electrons produced at different times. This conclusion is not surprising in itself, and has been involved implicitly in some of the theories of time lag that have been proposed. But one further point must be examined. In paper II it was urged that a denial of the assumption of independence was inconsistent with the ascertained fact that the mean current through a gas-filled cell, produced by a given light beam interrupted by a rotating disc, is independent of the speed of rotation.

The evidence for the supposed fact was therefore re-examined. The mean current through the cell was measured by a galvanometer, while the speed of the disc was varied so that n, the frequency of interruption, ranged from 200 to 8000 per second; the greater part of the current was compensated by a second cell. Sensitivity was limited by the continual change of current under a constant light, characteristic of all gas-filled cells used at a high gas factor; nevertheless undoubted changes of the mean current were observed. They varied greatly in amount; the previous failures to detect changes were due to the unfortunate selection of a cell in which they were particularly small, and to the use of small mean currents.

$\bar{\imath}_1$ Table 1 gives some results. In the fifth column $\bar{\imath}_1$ is the mean current at $n=8000$
$\bar{\imath}_2$ and $\bar{\imath}_2$ the mean current at $n=200$.

It is to be observed that $\bar{\imath}_1/\bar{\imath}_2$ is always less than 1 and decreases as either $\bar{\imath}$ or m is increased; there is no close correlation between $\bar{\imath}_1/\bar{\imath}_2$ and the time lag, but in any particular cell they increase together, as is to be expected. Some further observations on this matter are recorded in the next section. The value of $\bar{\imath}$ in the frequency-response curves of figures 5, 7 and 9 is that appropriate to $n=8000$; but in these curves the variation of $\bar{\imath}$ is negligibly small.

The only evidence for the theory that has been discussed is destroyed. With it goes a favourable approach to the problem of determining the physical processes underlying time lag; for if $f(\tau)$ existed and could be determined, it would be relatively easy to test various suggestions concerning these processes. This possi-

bility has to be abandoned. The rest of the paper deals with some miscellaneous experiments made in the hope of finding a clue to some other approach.

Table 1

Cell	Gas factor m	Mean current (μA.)	Time lag $i_a/\bar{i}$ ($n=8000$)	$(1-\bar{i}_1/\bar{i}_2)\times 100$
CMG 7 (large cylindrical)	10	4	·71	0·7
	10	2	·73	0·4
	5	2	·81	0·2
CMG 22 (small cylindrical)	9	6	·71	6·0
	9	1·2	·76	2·5
	4	7	·85	2·0
	4	2	·87	1·5
CMG 24 (spherical)	10	7	·52	7·0
	10	4	·54	4·0
	5	4	·77	1·7

§ 3. THE EFFECT OF THE SIZE OF THE CELL

The question how the time lag varies with the size of the cell is not determinate. For how are other relevant factors to be varied with the size, e.g. the gas pressure, the applied voltage and the current? It appeared that conditions might be comparable if the cells were all spherical, contained the same mass of gas, were operated at the same m, and at a current so small that time lag is independent of current. A series of spherical cells with cathode on the wall were made up, satisfying these conditions. But from the irregularity of the results it was concluded that some other factor must be varying, probably the nature of the cathode and possibly

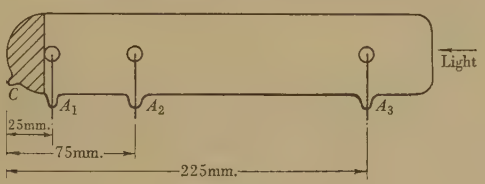

Figure 10.

impurities in the gas (see below); nothing could be concluded except that at the same gas factor the larger cell by no means always had the larger time lag.

In a second attempt a cell of the form shown in figure 10 was constructed and filled with argon. It will be seen that there are three small anodes A_1, A_2, A_3 at 25, 75, 225 mm. from the hemispherical cathode C covering one end of the cell. Many experiments were made with this cell; but only two need be recorded.

In one experiment two frequency-response curves were compared: (1) with A_1 as anode and A_2, A_3 connected to the cathode; (2) with A_3 as anode and A_1, A_2 connected to the cathode. The gas factor was the same ($m=10$) in both cases; the voltages applied to the anode to attain this gas factor were 111 V. in (1) and 206 V. in (2). Since the distance of A_3 from the cathode is 9 times that of A_1, the mean velocities of the electrons and ions must surely have been smaller in (2).

But figure 11, which gives the two frequency-response curves, shows that there was little difference in time lag; certainly at frequencies below 10,000, there is no evidence that time lag depends directly on the speed of any particle along the direction of the field. On the other hand it may depend on a speed of diffusion (e.g. of metastable atoms) perpendicular to the field; for the tube is of uniform bore.

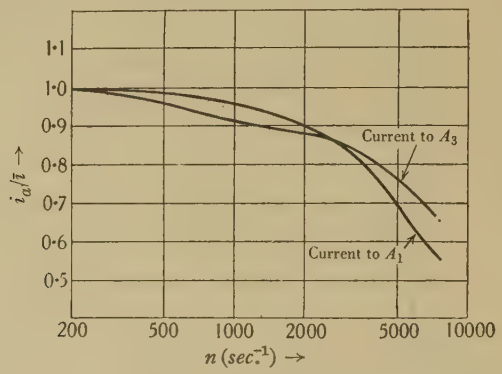

Figure 11. 4-electrode tubular cell, $m=10$, $i=2$ μA.

It may be added that the static characteristic and the frequency-response curve in the long cell were influenced greatly by shields surrounding it; as might be expected, charges on the walls affect the characteristic and through it the frequency response. On the other hand the spherical cells proved once more that these charges cannot be the main cause of low-frequency lag; for these cells had very small windows and very little bare glass, and yet some showed very marked lag.

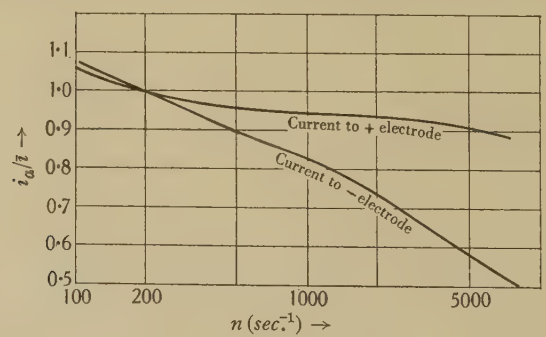

Figure 12. 4-electrode tubular cell.

In the second experiment, A_3 was the anode at 160 V., while A_1 and A_2 were maintained at -60 V. relative to the cathode; A_1 and A_2 then receive only positive ions; the current to A_1+A_2 was about 1/3 of that to A_3. The gas factor of the anode current was 4. The frequency response curves of the current arriving at A_3 and of the current arriving at A_1+A_2 are shown in figure 12; the time lag of the latter current is much the greater. This is, of course, to be expected; for positive ions must always be secondary and produced after the primary electrons; but it is well to be sure that the expected happens. No quantitative conclusions seem possible.

It is to be observed that the value of $i_a/\bar{\imath}$ is shown increasing above 1 at low

frequencies. This is because the mean current $\bar{\imath}$ rises rapidly at low frequencies; $\bar{\imath}$ is taken as the value at about $n = 1000$; it is actually greater than this value below $n = 200$, and $i_a/\bar{\imath}$ is not really greater than 1.

§ 4. TIME LAG AND TEMPERATURE

One of the facts recorded in paper II is the variation of the low-frequency time lag with the temperature of the cell. Since this variation was discovered only just before the previous experiments had to be interrupted, some more observations were made to confirm its reality; they were successful.

Although the total amount of gas in a sealed cell, and its average density, are unchanged when the cell is cooled, the distribution of the gas may be altered, for example by condensation on the cooled wall which carries the cathode. Accordingly it was important to discover how far the changes in time lag could be due to such changes. For this purpose a gas-filled cell was attached by a narrow tube to a bulb of approximately equal volume; frequency response curves were taken with (1) cell hot, bulb hot; (2) cell hot, bulb cold; (3) cell cold, bulb hot; (4) cell cold, bulb cold. ("Hot" means at room temperature, "cold" at liquid-air temperature.) The density of the gas in the cell, if there is no appreciable condensation on the

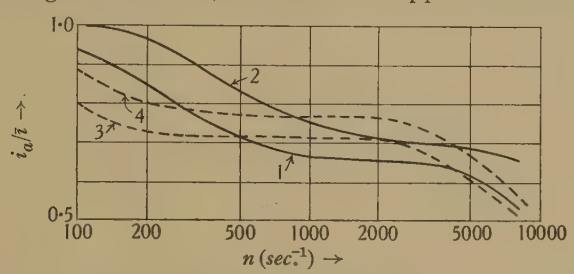

Figure 13. Variation of frequency response with temperature CMG 7 cell, argon filled, $m = 10$.

walls, should be the same in (1) and (4), but greater in (3) and less in (2). Condensation on the cathode-wall should be greater in (3) and (4) than in (1) and (2). The gas factor was adjusted to be the same in all cases; this involved change of the applied voltage.

The results are shown in figure 13, which gives the frequency-response curve for each of the conditions (1), (2), (3) or (4); the applied voltages being 83, 94, 72 and 76. The results indicate that at high frequencies the time lag is determined almost entirely by the density of the free gas in the cell; for at $n > 5000$, curves (1) and (4) are almost the same. But, as was found previously, the low-frequency time lag, indicated by the rate at which the curve falls initially, is greater when the cell is cold. This may be due to a change in the nature of the cathode due to condensation of the argon in it; this explanation, though possible, was not suggested in paper II. On the other hand it may be due to a change in some diffusion process in the gas, as suggested in paper II. These experiments do not enable a distinction to be made, but they confirm very clearly the distinction, made in paper II, between low-frequency and high-frequency time lag; it is clear that one can vary greatly without any great change on the other.

§ 5. EFFECT OF HYDROGEN ON THE TIME LAG

It has long been recognized that cells of the Elster-Geitel type, with cathodes of sensitized potassium, show very much less time lag than modern cells with cathodes of the type Ag-O-M, especially when M is caesium. Since the same gas, argon, is used for filling cells of both types, it has been naturally concluded that the greater time lag of the modern cell is connected with its cathode.

But among the facts recorded in paper I are some observations on *un*sensitized potassium cells; it seemed that these had a time lag much greater than that of the sensitized cells and comparable with that of Ag-O-M cells. But, since the geometrical form of the cells compared was not always the same, the result was not regarded as conclusive.

The matter has been re-examined and the previous result confirmed. Even if the cells are geometrically similar and filled with the same gas at the same pressure, the unsensitized cell shows a marked low-frequency time lag, while the sensitized cell shows none; and even at high frequencies the frequency-response curve is steeper in the unsensitized cell. If this difference were due to the cathode it would be very difficult to explain, for in every apparently relevant property the sensitized cathode resembles the Ag-O-M cathode more nearly than the unsensitized. However it appeared that this difference might not be due to the cathode. Sensitized cells always contain a trace of hydrogen; for some of the hydrogen absorbed in sensitization is slowly liberated later until an equilibrium pressure is reached. Ag-O-M cells never contain hydrogen, for the gas is fatal to their sensitivity. Unsensitized cells are also free from hydrogen, for the unsensitized metal absorbs, rather than liberates, hydrogen. The low time lag of sensitized cells might be due to a trace of hydrogen in the gas.

Accordingly, a cell with a potassium cathode filled with argon was provided with a palladium tube through which hydrogen could be introduced and removed. The series of frequency-response curves shown in figure 14 was obtained; the scale of n is plain, but logarithmic. All were taken at the same m (which means different voltages) and about the same $\bar{\imath}$; ϕ is the primary emission from the cathode in $\mu A/L$ for light at 2800° K.

Originally the potassium was unsensitized and no hydrogen was present; there is large low-frequency lag and low emission (*a*). When a little hydrogen was added, the lag decreased greatly; the emission was also greatly decreased (*b*). After 18 hours the emission had increased again, but the lag had decreased further and indeed almost vanished (*c*); but after 72 hours, much of it had reappeared (*d*). The changes (*c*) and (*d*) may be attributed to absorption of the hydrogen by the cathode, which however retained the metallic appearance of the unsensitized metal.

A considerable quantity of hydrogen was now introduced and a discharge was passed, so that the cathode acquired the colour characteristic of the sensitized metal and the emission increased. The hydrogen was removed; the time lag was considerable (*e*); after 48 hours, during which hydrogen was probably evolved, the time lag was less (*f*); by adjusting the quantity of hydrogen by trial, a curve approaching (*b*) could be obtained.

These and similar experiments prove conclusively that the presence of hydrogen in relatively small quantities affects the time lag profoundly. The difference between (*a*) and the remaining curves suggests that part of the difference may lie in gas absorbed on the cathode; for if hydrogen was absorbed between (*a*) and (*b*) it would not be removed by subsequent events. The next step is clearly to deter-

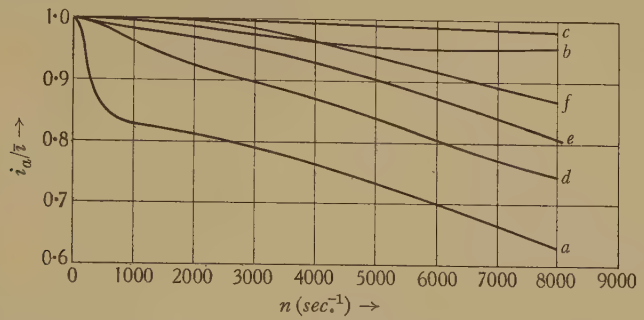

Figure 14. Effect of hydrogen. (*a*) to (*d*) cell unsensitized. (*a*) no hydrogen, $\phi = 0{\cdot}33$; (*b*) on addition of hydrogen, $\phi = 0{\cdot}05$; (*c*) 18 hours after addition of hydrogen, $\phi = 0{\cdot}03$; (*d*) 72 hours after addition of hydrogen, $\phi = 0{\cdot}42$; (*e*) on sensitization of cell and removal of excess hydrogen, $\phi = 0{\cdot}80$; (*f*) 48 hours later, $\phi = 0{\cdot}90$.

mine quantitatively the hydrogen present at the various stages; but the determination is attended by some experimental difficulties which had not been surmounted when the work had to be interrupted. Further examination is therefore deferred. But it may be observed that, except when the cathode was being sensitized—for instance between (*d*) and (*e*)—the amount of hydrogen present was always too small to affect the colour of the discharge; the argon must always have been ionized, and there was much evidence that the time lag was a minimum for some optimum amount of hydrogen, and greater for either greater or less amounts.

§ 6. DISCUSSION OF RESULTS

All the frequency-response curves in these experiments were taken at frequencies less than 10,000. They all confirm the view that the low-frequency time lag, operative at these frequencies, is distinct from the high-frequency lag operative at 20,000 c./sec. and upwards. Further, Roggendorf[3] has shown that at sufficiently high frequencies time lag eliminates all but the primary photoelectric current, so that $i_a/\bar{\imath} = 1/m$. As was pointed out above, there is no sign in these experiments of an approach to this limit. Again it may be taken as certain that the high-frequency time lag is due partly, if not wholly, to the finite velocity of the ions and to the time that they take to travel between the electrodes[3, 4, 5]*. It follows that this finite velocity is not responsible for the low-frequency lag.

As an explanation of low-frequency lag, the presence of metastable atoms, suggested by Schroeter and Lubszynski[6], is plausible, as was indicated in § 3. However, there are some difficulties.

* In view of the criticisms of Kvartskhava and Timofeev it may be well to point out that we have never denied that the high-frequency lag is due to this cause; our remarks applied only to the low-frequency lag. Their experiments, in which they assume that there is no time lag below 1000 c./sec. throw no light on this lag.

Schroeter and Lubszynski suggested that the smaller time lag in argon, as compared with neon and helium, might be due to effect of impurities on the metastable states of this gas; the experiments described in § 5 might seem to support this view. But we are not clear that hydrogen should have the effect they suggest. Penning's theory, universally accepted, of the effect of hydrogen in changing the sparking-potential (and other electrical properties) of neon and helium rests on the fact that the ionization potential (16·1 V.) of hydrogen is less than the energy of the metastable states of neon (16·5 V.) and of helium (19·8 V.). But the energies of the metastable states of argon (11·5 and 11·7 V.) are less than the ionization potential of hydrogen, which is also greater than the ionization potential of argon (15·4 V.). It is not obvious why the presence of a small quantity of hydrogen in a large quantity of argon, of lower ionization potential, should have any effect in destroying the metastable states of the latter. However Penning[9] has stated, as a fact, that hydrogen has this effect on argon.

Moreover, if metastable states disappear, with the production of charged carriers, by reaction with the unionized gas or with the walls, any time lag due to metastable states should accord with the assumption of independence; the products of successive light impulses should interact only if the metastable atoms react with charged carriers or with each other. The proof that this assumption is false is not easy to reconcile with any simple theory that attributes time lag to metastable states.

The remaining theories proposed are those of Fourmarier[7] and Kingdon and Thomson[8]; the former associates time lag with ionization by positive ions, the latter with thermal changes produced in the cathode by the impact of positive ions. The former is either a variant of Ollendorf's theory, or requires us to suppose that the individual ionizations by positive ions take time—a supposition for which there is no evidence. The latter theory, not very definite in any case, does not seem easily reconcilable with the experiments described in §§ 4 and 5.

We do not propose to put forward any theory of our own, for though there is evidence that the nature of the cathode, and particularly gas absorbed on it, has some effect, none of the obvious explanations of that effect seem satisfactory. Our object is rather to insist that the facts concerning low-frequency time lag are much more complicated than has been generally recognized; that none of the theories proposed hitherto take account of the complexities, and that many more experiments will be required before any new theory can be tested adequately.

REFERENCES

(1) Campbell, N. R. and Stoodley, L. G. *Photoelectric Cells and their Applications*. Joint discussion of the Physical and Optical Societies, June 5th, 1930, p. 64.
(2) Campbell, N. R. *Phil. Mag.* (7), **14**, 465 (1932). The notation used here is slightly different from that of this paper.
(3) Roggendorf, A. *Phys. Z.* **36**, 660 (1935).
(4) Ollendorf, F. *Z. Phys.* **13**, 606 (1932).
(5) Kvartskhava, I. and Timofeev, P. *Tech. Phys. U.S.S.R.* Part 4 (1935).
(6) Schoeter, F. and Lubszynski, G. *Phys. Z.* **31**, 897 (1930).
(7) Fourmarier, P. *C.R. Acad. Sci.*, Paris, **194**, 86 (1932).
(8) Kingdon, K. H. and Thomson, H. E. *Physics*, **1**, 343 (1931).
(9) Penning, F. M. *Phil. Mag.* **7**, 963 (1931).

DISCUSSION

Mr L. Treloar. In connexion with the theory that attributes the time-lag to the presence of metastable atoms, one of the authors stated that such atoms, on striking the cathode, were supposed to give rise to the emission of secondary electrons. Is there any evidence to suggest that secondary emission would in fact take place as a result of such a process?

Authors' reply. It is theoretically probable that the energy stored in metastable atoms is available to liberate electrons from the atoms of solid bodies as well as from the atoms of gases; we believe that there is some experimental evidence for such liberation, but "secondary emission" may not be an appropriate term for it. If, as de Boer holds, photoelectric emission from composite cathodes is photo-ionization of adsorbed atoms, surely the ionization of such atoms by collisions of the second kind is almost inevitable.

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THE RELATION BETWEEN RATE AND ARC FOR A FREE PENDULUM

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ABSTRACT. When a pendulum swings about a centre in a vacuum the well-known circular deviation gives the increase of period with amplitude. For the case in which the pendulum is suspended by a spring the period has been calculated but not the change with amplitude. The presence of air increases the period in three ways: for two of these the amount has not been computed and may depend on amplitude. Thus for the ordinary clock pendulum, apart from the effect of the impulse, experiment is necessary to compare the real amplitude deviation with the computed circular deviation. In about 1856 J. M. Bloxam recorded a change of rate between two amplitudes of only one-half the circular difference. The writer, on the other hand, has found five rates which fit the circular deviation within less than 1 per cent.

§ 1. AMPLITUDE, CIRCULAR AND IMPULSE DEVIATIONS

THE experiment described in §§ 4 to 17 of this paper gives reliable results, for one pendulum at least. Many horologists may be doubtful about observations made with a variable temperature, but other observations proved that, with the pendulum used, the effect of temperature on rate could be accurately allowed for (§ 16). Temperature-control would not have added materially to precision since the weakest link in the experimental chain is the decrement-determination (§ 13). Judgment was needed in drawing the smooth curve from which values were to be read for computing impulse deviations. This judgment was not biased by the general result of the experiment as it was exercised before I realized what this result would be.

By amplitude deviation I mean the loss in seconds per day of a free pendulum, α when swinging through a finite arc 2α radians, which keeps true time when the arc is infinitesimal. A constituent of amplitude deviation is circular deviation* computed on the assumption that the centre of gravity moves in a circle. If the maintaining impulse of a clock imposes an impulse deviation on the pendulum, relative values of amplitude deviation are found by deducting impulse deviation from observed clock rates. "Amplitude"† means the semi-arc α.

Prof. R. A. Sampson, referring to amplitude deviation in *Studies in Clocks and Time keeping*[1], says that he "reserves the question whether this quantity is ade-

* Often called "circular error". It seems preferable to use "error" to mean change of rate due to unit change of α. Then the error is the differential coefficient of the deviation with regard to amplitude.

† Unfortunately, "arc" and "semi-amplitude" also are used for α in clock literature.

quately represented by circular deviation." When the pendulum turns about an ideal knife-edge (see § 18) and swings *in vacuo*, no such reservation is necessary. Rate then changes with arc solely because the centre of gravity moves in a circle so that central acceleration is proportional, not to an angle, but to its sine. The circular deviation is easily computed[2]. For amplitudes up to 2° the circular deviation = 86,400 $\alpha^2/16$ to the nearest millisecond per day.

§ 2. SIMPLE CIRCULAR DEVIATION DOES NOT NECESSARILY APPLY TO A SPRING-SUSPENDED PENDULUM MOVING IN AIR

When the pendulum is suspended by a spring, this adds to the restoring moment due to gravity. Moreover the centre of gravity no longer moves in a circle. Sampson gives the theory for a uniform spring[3], but he rejects powers of angles above the first in solving the equations, so that no light is thrown on amplitude deviation.

The air or other medium in which the pendulum moves increases the period in three ways. (*a*) Buoyancy reduces the effective weight. This does not affect amplitude deviation as the rate-change is independent of α. (*b*) The air is in motion so the effective mass of the pendulum is increased. The consequent increase in period varies with the shape of the pendulum and its surroundings and it is likely to change with amplitude. (*c*) It is often stated that air resistance has a negligible effect on the period and this would be true were it symmetrical about the vertical. The pendulum, however, moves in air which it has already disturbed, so resistance at any angle before the central position is reached is greater than that at an equal angle after that point, and air resistance consequently increases the period. It is, at least, not evident that the increase is the same for all amplitudes.

Thus, for the ordinary clock pendulum experiment is necessary to compare the real amplitude deviation with the computed circular deviation and the result applies strictly only to the pendulum used and the surrounding conditions (enclosure, air-density and temperature) obtaining during the experiment.

§ 3. SHORTT ERRORS COMPARED WITH CIRCULAR DEVIATION. BLOXAM'S EXPERIMENT

Amplitude deviation is of practical as well as theoretical interest. Thus with a gravity impulse the working conditions should secure that, for a small change in the moment, the fall in impulse deviation will balance increase in amplitude deviation. The irregularities in rate of two Shortt Clocks at Greenwich have been compared with the circular errors[4] (SH_{11} during 10 months, 1926–7, SH_3 during 22 months, 1928–9) showing fair agreement for three-quarters of the time. This throws no light on amplitude deviation, since no estimate is made of the effect of the impulse on rate, and indeed the causes of the amplitude-changes were unknown.

Nearly eighty years ago J. M. Bloxam tried the only amplitude deviation experiment of which I have read. He designed a gravity escapement and applied it to a clock (still going in the Science Museum, South Kensington) which G. B.

Airy described in 1856 as "a better clock than I have ever used as far as I remember". This type of escapement was used by E. B. Denison for Big Ben.

Bloxam experimented with this clock in Madeira between 1854 and 1857 and changed the amplitude from 89 to 115 min. in 1855 or 1856. No details of observations seem available. After the increase of amplitude Bloxam added $1\frac{1}{4}$ lb. of mercury to the bob, as compensation proved deficient at the larger amplitude. After Bloxam's death Airy published[5] the bare result that "after deducting the estimated effect of the action of the escapement there was a difference of rate of 1·24 sec./day, about half the difference of the circular errors" [2·42].

§ 4. THE AUTHOR'S EXPERIMENT ON PENDULUM 11

During the last eight years I have been experimenting with a series of pendulums enclosed in sealed cases and impulsed by gravity levers. In 1930 I fitted a contrivance to one of the brackets for changing the impulse in order to repeat this experiment under modern conditions. For this purpose I used Pendulum No. 11 during March to May, 1934. This pendulum, in spite of faults, is very stable and, as the result showed, behaved well during the experiment. The general principle is very simple. This and the results obtained will be described before details about methods of observation and reduction and other matters are given.

Clock rates were found by comparing time with the Greenwich 10-h. rhythmic signal radiated from Rugby. About half an hour earlier, observations were made each morning of amplitude, pressure and temperature in the sealed case. For a period lasting from 4 to 9 days, during which the impulse had the same value, the mean rate was recorded together with the averages of the other observations. For a new period, the impulse was changed and observations commenced on the following morning.

In order to change the impulse air must be admitted to the case and be pumped out again, so that the air-density was not exactly the same for each period. The densities are proportional to the pressures (read on an aneroid barometer) reduced to the standard temperature of 60° F. The reduced values were those recorded.

§ 5. THE OBSERVATIONS

The observations relating to the eight periods which constituted the experiment are recorded in table 1. The rates there given are, however, not the observed ones, which appear in the first column of table 4. In order to avoid detail at this stage the rates given relate to standard working conditions of air-density and temperature, etc. A rate is + when the clock is gaining. Two thermometers are used. Temperature in the table is that given by the lower one with its bulb just above the bob. Stratification is excess of upper thermometer temperature over lower (see § 15).

Periods are numbered in the order in which experiments were made. Amplitudes were increased from about 40 to 70 min. and it should be noted that observations on 29 min. follow immediately after those for 70 min. and that at the finish (periods

6 to 8) the amplitude is back again around the initial value (too much of the time was devoted to this amplitude). In this way secular change in rate is best detected and least harmful.

Table 1. Observations

Period	Duration (days)	Temperature (°F.)	Stratification (°F.)	Barometer (inches)	Rate* (sec./day)	Amplitude (minutes)
1	9	61·0	1·93	21·315	0·068	39·78
2	4	61·0	2·07	·302	0·600	51·18
3	7	61·3	2·01	·360	1·022	61·60
4	6	67·7	1·77	·290	1·331	70·24
5	6	64·8	1·80	·290	−0·723	29·33
6	5	65·8	1·90	·266	−0·080	37·89
7	4	66·2	1·92	·362	0·012	39·21
8	8	68·3	1·96	·256	0·142	41·19

* Reduced to standard conditions. See table 4.

§ 6. ELIMINATION OF IMPULSE DEVIATION

In table 2 periods are arranged in order of amplitude. The impulse adds the seconds per day shown in column 2 to the free pendulum rate, so that this latter is found by subtracting impulse deviation from clock rate leaving a *losing* rate shown in column 3 which is to be compared with circular deviation (column 4).

Table 2. Reductions (seconds per day)

Period	Gaining rates	Losing rates			
	Impulse deviation	Free pendulum	Circular deviation	Residue	
5	0·775	1·498	0·393	1·105	
6	1·699	1·779	0·656	1·123	Weighted mean 1·097 at 39·71 min.
7	1·821	1·809	0·703	1·106	
1	1·876	1·808	0·723	1·085	
8	2·005	1·863	0·775	1·088	
2	2·899	2·299	1·197	1·102	
3	3·846	2·824	1·734	1·090	
4	4·671	3·340	2·255	1·085	

The clock was regulated for zero rate with amplitude about 39 min. Had it been regulated to gain 1 sec./day all the free pendulum rates would have been smaller by 1: we are concerned not with the rates but only with their differences. To find how far spring and air modify the circular deviation, the next step is to deduct this from the free pendulum rate. In view of Bloxam's results here comes the surprise; the result is about 1·1 sec./day in every case. In other words, the rates found by experiment fit the computed circular deviation values.

This is shown in table 3, where the true value of the residue has been taken as 1·102 sec./day, which has been subtracted from all the free pendulum rates.

The table shows that no value of amplitude deviation differs from the corresponding circular deviation by as much as 1 per cent. It is not quite correct to

label these first quantities "amplitude deviation" because this assumes that the corresponding quantity for infinitesimal amplitude would be 0. Just as Bloxam gets one difference from observations on two amplitudes so here I get *four* results from *five* amplitudes, which fit in with circular deviation.

Table 3. Free pendulum (seconds per day)

Amplitude	Amplitude deviation	Circular deviation	Difference
29·33	0·396	0·393	+0·003
39·71	0·716	0·721	−0·005
51·18	1·197	1·197	0
61·60	1·722	1·734	−0·012
70·24	2·238	2·255	−0·017

Amplitude deviation appears to grow slightly less rapidly with amplitude than circular deviation. No importance can, however, be attached to the differences shown in the table since they are possibly due to inexact values of decrement (§ 13)

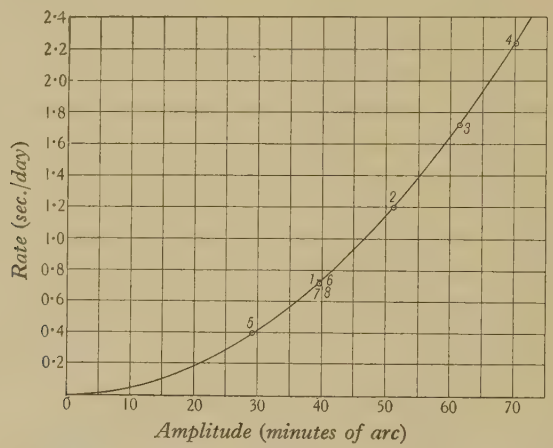

Figure 1. Amplitude deviation. The curve is the *computed* circular deviation. The points are *observed* amplitude deviations.

used in calculating impulse deviation. Changes in δ of less than 0·5 per cent would wipe out all the differences.

The results are shown in figure 1. It must be remembered that the curve is not a smooth curve drawn through the points but a computed curve with which the points derived by experiment are to be compared.

§ 7. RESULT FOR FREE PENDULUM

Thus the resultant contribution to amplitude deviation of the three factors referred to in § 2 is negligible, but it does not follow that the contribution of each is zero. Consequently another pendulum might yield a different result.

Pendulum 11 has a gun-metal bob 7·4 cm. in diameter, 16·0 cm. high, and weighing about 5740 g.; and an invar rod 0·8 cm. in diameter weighing 440 g. The

Elinvar suspension spring is 1·08 cm. long and 1·27 cm. wide. It is mostly 0·0137 cm. thick but is heavier at the top. The pendulum is housed in a cylinder about 20 cm. in diameter. Case and pendulum are carried on brackets bolted into $2\frac{1}{2}$ cwt. of concrete keyed into a 14-in. wall. Energy-dissipation is notably higher when the pendulum is in the case than when in the open. Some details of the experiment will now be given.

§ 8. DETAILS OF EXPERIMENT

"Amplitude" for a pendulum turning about a centre can mean but one thing, but that is not so with a suspension spring. In practice a linear displacement is observed and this is converted into angular measure by dividing by a radius. From what centre shall the radius be measured? One reasonable choice would be the centre of curvature of the path of the centre of gravity. I make another choice by regarding amplitude as the maximum inclination of the rod to its mean position. In this case the centre is the intersection of the moving rod with its rest position, a point for pendulum 11 about 1·4 mm. below the centre of curvature. Accurate measurement of amplitude in this experiment is necessary not only to relate it to the clock rate but also for finding decrement and impulse angles in order to compute impulse deviation. Adequate arrangements are not usually made for this measurement with precision clocks.

§ 9. SCALE-READING BY MICROMETER

I read the scale (which is situated on the top of the bob) by means of a micrometer eyepiece placed above the top plate of the case. For this purpose a plate-glass window is provided in the brass plate and a lens 34 cm. below forms an image of the scale in the focal plane of the eyepiece. The index is a sharp V and is moved by means of a screw whose head is divided into 100 parts, 53 corresponding to a minute of amplitude. A reading is obtained by setting the index first on a scale division at one extremity of the swing and then on another division at the other extremity. The angle between the two scale divisions and the difference between the readings on the micrometer head combine to give the amplitude. For accurate setting it is necessary to observe a scale line several times as it flashes into its stationary position. The amplitude can then be read to 0·01 min., say half a second of arc. When amplitude is changing, as in measuring decrement (§ 13) or angle of impulse (§ 12) or with pendulums which are not impulsed each cycle, determinations must be made rapidly and the results are less precise.

The ivory scale is illuminated by a lamp placed outside the glass cylinder of the case. This scale contracted 0·7 per cent after being placed in the dry air of the case but its dry length has not changed to a readable extent (0·02 per cent) during 4 years. The observed reading is reduced to true minutes by correcting for ruling errors and then deducting 1·1 per cent, corresponding to a distance 92·07 cm. of scale from the turning point.

§ 10. METHOD OF READING WITH BRIGHT LINES

Another kind of scale, which I adopted in 1932 for bracket *F* (which is used for testing half-second pendulums) makes the reading of amplitude more rapid. This is one of Julius Rheinberg's beautiful grainless graticules, a negative with transparent lines on an opaque field. A beam of light, entering the case through the micrometer window, is twice reflected so as to pass through the scale up to the micrometer. To set on a line, the index is moved until its tip is just visible on the background of a bright line in its stationary position. There is no need to judge of coincidence: you either see the tip or you do not. Allowance is made for the fact that the setting is near the edge of the line instead of its centre. This system is better suited for measuring the changing amplitudes referred to above[6].*

§ 11. THE IMPULSE

Motion is maintained by an impulse lever in connexion with an armature arm moved by an electromagnet between a front stop and a back stop[7]. When the impulse lever is not moving with the pendulum it is supported by the armature arm, which is then against its front stop. When the pendulum has swung through an angle θ_1 to the left it picks up the lever and carries it forward up to full amplitude

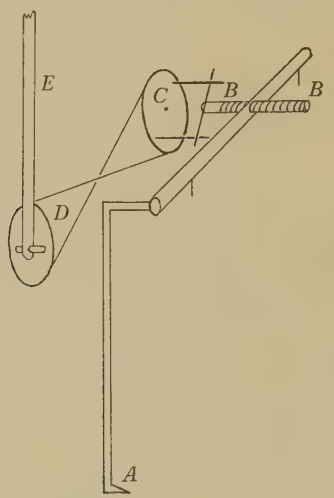

Figure 2. Impulse changer.

and back again. Meanwhile the arm has moved to its back stop, which is adjusted so that the lever is not removed from the pendulum until this has reached angle θ_1 to the right. The extra movement to the right through $2\theta_1$ enables the lever to deliver energy to the pendulum. The arm returns the lever to the initial position ready for a repetition of this cycle of events.

* Mr F. Hope-Jones (*Electric Clocks*, p. 226) says that the semi-arc of the Shortt pendulum falls 6 seconds per half-minute. The fall is really only about one-quarter of this, supposing the data of the preceding paragraph to apply to a 7-kg. pendulum with 54 min. semi-arc.

The magnitude of the impulse can be varied by means of a screwed horizontal arm of the lever. Figure 2 represents the lever which presses on the pendulum at A, B being the horizontal arm. Two coupled pulleys C and D are also shown with a rod E operating D by means of a crank.

To change the impulse, air is admitted to the case and the glass is removed from the micrometer window. The rod is inserted through the window and the pulleys can thus be turned. Pulley C, facing B, has two wires parallel to its axis which engage with a cross wire at the head of B. Thus B is turned and a small reverse motion of the crank clears the lever of the pulley wires. The case is then sealed and the pressure is reduced as nearly as possible to its former value.

§ 12. IMPULSE DEVIATION

The impulse deviation is $86{,}400\,\delta \cot \tau/2\pi f$ [8], δ being the decrement (§ 13) of the pendulum while $\sin \tau = \theta_1/\alpha$ and f is the frequency, which is $\frac{1}{2}$ for a seconds pendulum. This omits a small rate common to all amplitudes and another rate due to the inertia of the lever amounting to 0·005 sec./day for an amplitude of 40 min. and to 0·004 for the rest. θ_1 was measured by finding the smallest amplitude at which impulsing takes place. Since the armature does not commence to move instantly on make and break of current the value found for θ_1 (26·35 min.) is more likely to be too large than too small. A better way is to use the telephone signal which is audible for changes far too short to move the arm. A small error in θ is not serious since it affects computed deviations all in the same direction but not, of course, to the same extent. δ

§ 13. LOGARITHMIC DECREMENT

Elementary theory supposes that a pendulum experiences resistance proportional at all times to its velocity. In accordance with this, amplitude drops from α_0 to α in t seconds where $\alpha/\alpha_0 = e^{-\delta t}$, the logarithmic decrement δ being a constant whose value could be found very exactly by observing the time (about 14,000 sec.) needed for amplitude to fall from 80 to 30 min.

In reality, resistance grows faster with velocity than this theory supposes, and δ is not a constant but increases slowly with α, as appears in figure 3. It is necessary, therefore, to observe smaller intervals (400–1500 sec.) needed for small changes (say $2\frac{1}{2}$ min.) of α. Measurements are made by cutting off the supply of energy to the pendulum and setting the micrometer index symmetrically so that scale lines, one at each end of a swing, pass equal distances beyond the index. These distances decrease until finally the lines coincide with the index, one immediately after the other, at time t_1 when the amplitude is α_1. Similar observations are made when the amplitude has fallen about $2\frac{1}{2}$ min. to α_2 at time t_2, and so on.

The value of δ adopted for α_2 is $(\log_e \alpha_1 - \log_e \alpha_3)/(t_3 - t_1)$. A value for α_3 is similarly obtained from observations of α_2 and α_4. Points on figure 3 represent the corresponding values of δ/π and the smooth line is used to provide values for computing the impulse deviations.

Owing to the difficulty of judging coincidences promptly it is not to be expected that the points will lie neatly on a line but, after making observations which seem satisfactory, one is disappointed to find how far the points spread. I have experienced this disappointment many times. It is a curious fact that the points are not distributed at random—a simple, wavy line can be drawn through, or very close to, all the points. Each wave is completed in 57 min. of the experiment, just as if a second pendulum of nearly equal frequency were attached to the bracket.

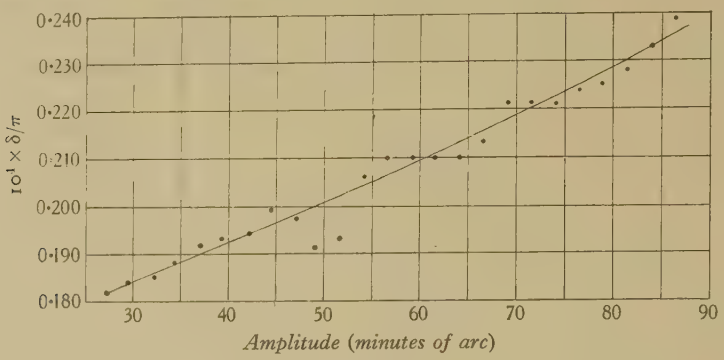

Figure 3. Decrement pendulum no. 11 at 21·3 sec. and 67° F.

§ 14. GENERAL UTILITY OF DECREMENT OBSERVATIONS

I find it difficult to understand why references to decrement experiments are so rarely to be found. In this way an accurate value can be found for the rate at which a pendulum dissipates energy, yet we find Denison[9] (later Lord Grimthorpe) equating this to the input by the driving weight—thus saddling the pendulum with train friction and deducing a value two or three times too large.

By decrement observations losses can be compared, for example, under different conditions of air and enclosure and different kinds of suspension and bracketing. By comparing decrements of long and short pendulums (using the same bob and spring) and of bobless pendulums of different lengths, I have found the contributions which bob, rod and suspension make to the total loss of energy. The result may have some bearing on the question whether long or short pendulums make the better timekeepers.

§ 15. TEMPERATURE AND STRATIFICATION

Temperature is read to 0·1° F. on a thermometer whose bulb is 2 cm. above the bob and on another one 67 cm. higher up. During the experiment the mean of consecutive morning readings of the lower thermometer was used for the compensation-correction for the intervening interval. Of course, this mean is not the average for the day, since the temperature goes through a cycle of changes in the time: the only defence for using it is based on the assumption that it was about as much below the average one day as another during the time of the experiment.*

* Since November, 1934, temperature has been recorded thrice daily.

The amount by which the reading of the top thermometer exceeds that of the other is a measure of Stratification. In a sealed case this is never absent and it has important effects on rate. Compensation in the region of the bob corrects for change of length of rod and change of elasticity of the spring. Increase of the temperature-gradient reduces the compensation. Moreover, the air-density increases below the centre of the case at the expense of the air-density higher up, and this slows the rate.

I am surprised that more attention is not given to stratification for precision clocks. I believe these are not always provided with the means of measuring it. It is often supposed that a fan used to blow warm air on to a case (usually bracketed to a wall or pillar cooler than the air) will prevent stratification inside.

§ 16. PRECISION WORK WITHOUT CONTROLLED TEMPERATURE

It will be noticed that this experiment was made with a clock whose temperature was not controlled (actually it varied by 11° F.). After experimenting with a Rieffler pendulum, Sampson states that "the correction of the mechanism of a clock for changes of temperature is, for fine work, a delusion"[11]. Results obtained with my pendulums between 1927 and 1931 pointed to a similar conclusion. Then in 1931 to 1933 I tried two pendulums in which the relation between rate and temperature was simpler, but it was necessary to allow for lag: the rate was higher for a rising temperature than for a falling one, apart from any correction for incomplete compensation. Finally, with pendulum 11 (used for this experiment) and pendulum 14 (under test in 1935) I cannot detect lag: it is sufficient to correct for over-compensation and stratification.*

Table 4.† Rate reduction (milliseconds per day)

Period	Observed	Greenwich	Compensation	Stratification	Acceleration	Barometer	Reduced
1	157	−3	− 50	−1	−41	+ 6	68
2	697	−4	− 50	+1	−45	+ 1	600
3	1100	0	− 54	0	−48	+24	1022
4	1517	+4	−131	−3	−52	− 4	1331
5	−567	+4	− 96	−3	−57	− 4	−723
6	108	−5	−108	−1	−60	−14	− 80
7	170	−6	−113	−1	−63	+25	12
8	365	0	−138	−1	−66	−18	142

† Observed rates by comparison with 10-h. signal; Greenwich corrections from *Notices to Mariners*; compensation reduced to 56·8° F. at −0·012 sec./day per ° F.; stratification reduced to 2·0° F. at +0·013 sec./day per ° F.; acceleration reduced to Jan. 1, 1934, at 0·0005 sec./day²; barometer reduced to 22·30 inches at 0·4 sec./day per inch.

§ 17. REDUCTION OF RATES TO STANDARD CONDITIONS

Table 4 shows the corrections applied to the observed rates to obtain the rates under standard conditions. The corrections to the Greenwich signals[10] are estimated after subsequent transit observations have indicated the general trend

* As regards pendulum 11, the evidence for this was accumulated during runs of 2½ months before the amplitude experiment and 8 months after it.

of the observatory clock rates. Stratification ranges from 0·5° F. in summer to 2·5° or even 3° F. in winter. It has only a small effect on the experiment as it ranged near to 2·0° F. all the time. The basic rate is assumed to have accelerated by 0·025 sec./day during the experiment. This is in accordance with observation during $2\frac{1}{2}$ months before the experiment and fits in with earlier and later determinations in the 40 min. region. After May, however, the acceleration had disappeared. An aneroid barometer is not a very satisfactory instrument for measuring pressure in a case: when pressure is rising with temperature, friction (which cannot be overcome by tapping) gives a low reading, and *vice versa*. Further, after being at atmospheric pressure, the barometer approaches true readings for lower pressures slowly, so that several days are needed to ascertain the proper barometric correction to rate.

§ 18. NOTE ADDED FEBRUARY 7, 1936

Dr Max Schuler's[13] experiences with pendulums supported on knife-edges show that it is necessary to distinguish between the material knife-edge and the ideal* one referred to in § 1. The latter consists of two surfaces cutting in a straight line about which the pendulum turns. The material edge is part of a cylinder rolling on a supporting cylinder. As the pendulum swings to the right the point of contact moves to the left, thus the arm of the restoring moment is increased and the frequency with it[12].

(*a*) When a right circular cylinder of radius r_0 rolls in another one of radius R_0 the extra arm is almost exactly $\rho_0 \sin\theta$ where $\rho_0 = R_0 r_0/(R_0 - r_0)$. In this case the principal term of the circular deviation is unchanged (see § 1). — ρ_0, θ

(*b*) If however ρ increases with θ, as when $\rho = \rho_0 + b\theta^2$, the extra arm increases faster than $\sin\theta$, and amplitude deviation is consequently less than circular deviation.

When $b = \frac{1}{2}(d + \rho_0)$, where d is the distance of the edge from the centre of gravity, the principal term of circular deviation is balanced out and the pendulum is nearly isochronous. — d

(*c*) A slight bend in the cylindrical edge makes it behave as if the central part were flat, so that the edge rocks over suddenly from one boundary of the flat to the other as the pendulum passes the vertical, producing a relatively large restoring moment for small values of θ, so that there is a rapid increase in frequency as small amplitudes decrease: see branch *OA*, figure 4.

Since these material edges are minute—say between 0·001 and 0·0001 in. in width—ρ_0/d is usually quite negligible. It would be difficult to observe the shapes of such edges and quite impossible to produce desired forms.

Figure 4 shows the result of observations made in 1930 by G. Th. Gengler in Dr Schuler's laboratory. The dotted line represents circular deviation and the full line the excess of amplitude deviation over this. Thus for 30 min. the amplitude

* Ideal is not here used as suggesting a quality to be desired as improving the time-keeping of a pendulum.

deviation $= 0{\cdot}95 + 0{\cdot}41 = 1{\cdot}36$ sec./day. The test was repeated in 1933 by H. Gräfe[14] who found that the deviation was unchanged, indicating that the knife-edge and support had resisted wear. This cylindrical edge either has a flattish face which makes contact with the support when $\theta \fallingdotseq 0$, or more probably it is slightly bent.

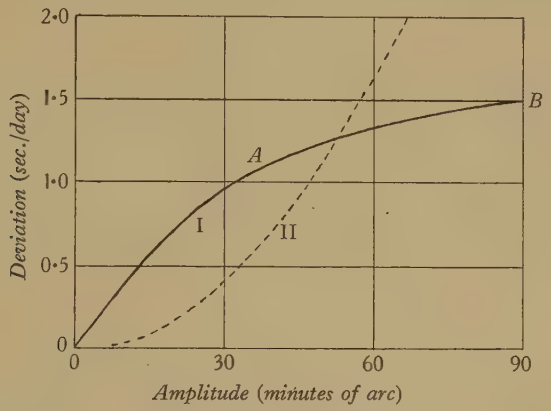

Figure 4. Deviations of Schuler pendulum with knife-edge suspension. I, Excess of amplitude deviation over circular deviation; II, circular deviation.

Such observations have been analysed by H. Gebelein[15], who has furnished a mathematical theory.

We thus reach this striking conclusion: although a spring-suspended pendulum can behave as if supported by an ideal knife-edge, a pendulum with a material edge has little chance of doing so.

REFERENCES

(1) Sampson, R. A. *Proc. roy. Soc. Edinb.* **38**, pt. 1, no. 11, p. 114 (1918); p. 105 for Cottingham.
(2) Sampson, R. A. *Proc. roy. Soc. Edinb.* **38**, pt. 2 (1918).
(3) Sampson, R. A. *Proc. roy. Soc. Edinb.* **38**, pt. 1, p. 86 (1918).
(4) Jackson, J. and Bowyer, W. *Mon. Not. roy. Astr. Soc.* **90**, No. 3 (1930).
(5) Airy, G. B. *Mem. roy. Astr. Soc.* No. 27 (1858).
(6) Hope-Jones, F. *Electric Clocks.* N.A.G. Press.
(7) Atkinson, E. C. *Proc. phys. Soc.* **42**, pt. 2, p. 63 (1930).
(8) Atkinson, E. C. *Proc. phys. Soc.* **42**, pt. 2 (equations 1, 6, 7, 14, 15) (1930).
(9) Denison, E. B. *Trans. Camb. phil. Soc.* **8**, pt. 5. On clock escapements (1849).
(10) *Admiralty Notices to Mariners*, Nos. 933, 1299, 1433 of 1934.
(11) Sampson, R. A. *Proc. roy. Soc. Edinb.* **44**, pt. 1, p. 59 (1924).
(12) Atkinson, E. C. p. 618 of this volume.
(13) Schuler, M. *J. Horolog.* p. 362 (Aug. 1935).
(14) Gräfe, H. *Z. Geophys.* Jahrg. 11, Heft 3, p. 146 (1935).
(15) Gebelein, H. *Ingen. Arch.* p. 75 (1935).

DISCUSSION

See page 621.

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ON AIRY'S DISTURBANCE INTEGRALS AND KNIFE-EDGE SUPPORTS FOR PENDULUMS

By E. C. ATKINSON, M.A.

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ABSTRACT. A century ago Airy employed two integrals to find the effect of a small disturbance on harmonic motion. More general use of these would have saved much effort in theoretical investigations. In the present paper the process is used to find the effect of a material knife-edge, consisting of a cylinder of any form rolling on another supporting cylinder, on the period and isochronism of a pendulum.

§ 1. THE DISTURBANCE INTEGRALS

In 1827 G. B. Airy[1] (afterwards Astronomer Royal) expressed the effect of a small disturbance of harmonic motion, which produces angular oscillation $\pi\sigma$ when the displacement is θ, in terms of two integrals $\int_0^{2\pi} \sigma \cos\tau\, d\tau$ and $\int_0^{2\pi} \sigma \sin\tau\, d\tau$ relating respectively to change of amplitude α and of frequency $n/2\pi$. τ is the phase of vibration: $\sin\tau = \theta/\alpha$. These integrals were used by Airy and by Denison[2] (Lord Grimthorpe) and more recently by Sampson[3] and David Robertson[4] in connexion with clock pendulums.

§ 2. SHOULD BE BETTER KNOWN

Much time and energy would be saved if these useful mathematical weapons were more generally recognized as such. Thus Bloxam[5], whose gravity escapement was used for the clock of the Houses of Parliament, wrote in 1853 on the theory of this escapement and of the dead-beat. He devised ingenious ways of getting his results at the expense of unnecessary labour to himself and to his readers.

By free use of Airy's method the second volume of Grossmann's[6] monumental *Horlogerie Théorique* could have been transformed. Not only would the analysis have been simplified but some of the results whose present form is so complex that the meaning can only be brought out by numerical examples would have automatically appeared in simple garb. Krebs[6] deals with the poising error of a balance wheel which is obtained as the sum of an infinite number of series. He gives only the outline of the reduction of this sum to the final series, yet this outline needs four pages. The Airy Integral $\frac{gh}{2\pi n^2 k^2 \alpha}\int_0^{2\pi} \sin\theta \sin\tau\, d\tau$ gives the result in a single line.

Gebelein[7] has dealt with the behaviour of a pendulum rolling on a so-called knife-edge. He reaches the general case in six stages occupying seventeen pages. All goes well until an error in the work of stage 5 makes the final formulae incorrect. The Airy solution is given in § 4 of this paper.

§ 3. EXAMPLE: CIRCULAR DEVIATION

I have discussed these functions elsewhere[8], but will show the use of the second one to obtain a result needed here. The simple equation of pendulum motion is

$$(d^2+k^2)\,\ddot{\theta} = -g\,d\,\theta, \qquad g$$

leading to

$$n = \sqrt{\frac{gd}{d^2+k^2}} \qquad \ldots\ldots(1),$$

mk^2 being moment of inertia about the centre of mass and d the distance from this point to the axis. For finite amplitudes, the restoring moment is $mgd\sin\theta$, so there is a correcting term to $(d^2+k^2)\,\ddot{\theta}$, namely $g\,d\,\theta^3/6$. m, k, d

$$\therefore \quad \pi\sigma = \frac{g\,d\,\theta^3}{6\,(d^2+k^2)}.$$

The Airy formula gives

$$\frac{dn}{n} = -\frac{1}{2n^2\alpha}\int_0^{2\pi}\sigma\sin\tau\,d\tau = -\frac{1}{12\pi\alpha}\int_0^{2\pi}\alpha^3\sin^3\tau\sin\tau\,d\tau = -\frac{\alpha^2}{16} \qquad \ldots\ldots(2).$$

§ 4. THE MATERIAL KNIFE-EDGE

The ideal knife-edge is a straight line forming an axis. The material edge is some form of cylinder rolling on another cylinder which supports it. Schuler[9] found that rate changed with amplitude, when pendulums were supported on edges, by no means according to circular law given in equation (2). Hence Gebelein's investigation.

Whilst the pendulum swings through θ to the left, the edge rolls to the position $O'A$ making contact with its support at A so that the arcs $O'A$ and OA are both equal to s. s

If r and R are the radii of curvature at A of edge and support respectively r, R

$$R\,d\phi = ds = r\,(d\phi + d\theta). \qquad \phi$$

$$\therefore \quad d\phi = r\,d\theta/(R-r) \qquad \text{and} \qquad ds = \frac{Rr}{R-r}\,d\theta = \rho\,d\theta, \text{ (say)} \qquad \rho$$

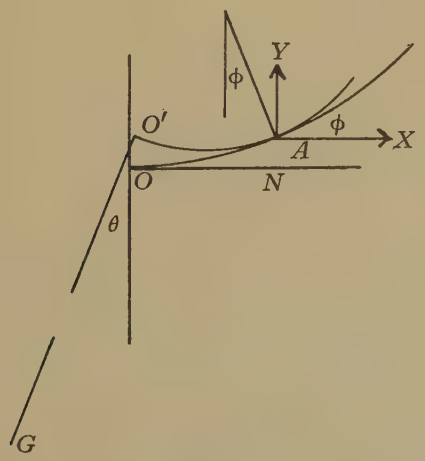


Figure 1.

Quantities of higher order (§ 6) being neglected, the equation of motion becomes

$$(d^2+k^2)\,\ddot{\theta} = -g\,(d\sin\theta + s) \qquad \text{.....(3).}$$

ρ_0, s_0 (*a*) If ρ everywhere $=\rho_0$, $s_0=\rho_0\theta$.

n_1
$$\therefore\quad n_1 = \sqrt{\frac{g\,(d+\rho_0)}{d^2+k^2}}\cdot\left(1-\frac{\alpha^2}{16}\right) \qquad \text{.....(4).}$$

In this case the rate is changed by the circular shape of the edge, but, if the small quantity $\rho_0\alpha^2/32d$ is neglected, the circular deviation is unchanged.

(*b*) If r and R are variable, s is larger than in (*a*) by $s-s_0$

$$\frac{dn}{n_1} = \frac{g}{2\pi n_1{}^2\,(d^2+k^2)\,\alpha}\int_0^{2\pi}(s-s_0)\sin\tau\,d\tau = \frac{4}{2\pi\,(d+\rho_0)\,\alpha}\int_0^{\frac{\pi}{2}}\cos\tau d\,(s-s_0)$$

$$= \frac{2}{\pi\,(d+\rho_0)}\int_0^{\alpha}(\rho-\rho_0)\cos\tau\,\frac{d\theta}{\alpha} \qquad \text{.....(5).}$$

This result is obtained by integration by parts and corresponds to Gebelein's equation (34).

§ 5. FORM FOR ISOCHRONISM

b Suppose $\qquad \rho=\rho_0+b\theta^2, \quad \therefore\ s=s_0+b\,\theta^3/3.$

Then
$$\frac{dn}{n_1} = \frac{2b}{\pi\,(d+\rho_0)\,\alpha}\int_0^{\frac{\pi}{2}}\frac{\theta^3}{3}\sin\tau\,d\tau = \frac{b\alpha^2}{g\,(d+\rho_0)}, \text{ as in § 3,}$$

$$n = \sqrt{\frac{g\,(d+\rho_0)}{d^2+k^2}}\cdot\left\{1-\left(1-\frac{2b}{d+\rho_0}\right)\frac{\alpha^2}{16}\right\} \qquad \text{.....(6).}$$

Here the growth of ρ with θ reduces the circular deviation. When $b=\frac{1}{2}(d+\rho_0)$ the pendulum is nearly isochronous.

§ 6. EFFECT OF NEGLECTED TERMS

In equation (3) quantities have been omitted as of higher order than those retained.

To estimate this order, I shall take the special case in which $R=\infty$ and suppose that $d=100$ cm. With R finite, s in equation (3) is too large by a quantity of order $s\theta^2$ or say 4×10^{-4} of itself for amplitude 0·02, i.e. 68 min. of arc. For isochronism $b=50$ cm., $b\alpha^2=0{\cdot}02$.

If $r_0=0{\cdot}06$, the edge will be about 0·002 in. wide, larger, I think, than is likely to be the case. This will make all r_0 terms larger than b terms and I use the former only in finding order of size. The coordinates (x, y) of O' are easily found to be $(r_0\theta^3/6, r_0\theta^2/2)$. The equation of motion found by the routine method of resolving vertically and horizontally, taking moments about G and eliminating X and Y, is

$$-(d^2+k^2)\,\ddot{\theta} = (g+\ \ldots\ +\ddot{y})\,(d\theta+\ \ldots\ -x)+(d\ddot{\theta}+\ \ldots\ -\ddot{x})\,(d+\ \ldots\ -y)$$

$$= -gx+d\ddot{y}\theta-dy\theta-d\ddot{x}+\ \ldots$$

where the omitted terms are introduced and the largest of the old ones retained,

$$d\,y\,\ddot{\theta} = d\,r_0\,\theta^2\ddot{\theta} = 100 \times 0{\cdot}06 \times \tfrac{1}{2}\,(0{\cdot}02)^2 \times n^2\,(0{\cdot}02) = 2{\cdot}4 \times 10^{-4} \text{ since } n^2 \doteqdot 10,$$

similarly for the other terms. All are of order 10^{-4}, whereas the principal term $gd\theta$ is of order 10^3, the circular deviation term $gd\,\theta^2\,6$ of order 10^{-1}, and gs between 1 and 10^{-1}. Thus the small term given by equation (5) may be regarded as correct to 1 in 1000 for a normal edge.

REFERENCES

(1) Airy, G. B. *Trans. Camb. phil. Soc.* **3**, pt. 1 (1827).
(2) Denison, E. B. *Trans. Camb. phil. Soc.* **8**, p. 633 (1849).
(3) Sampson, R. A. *Proc. roy. Soc. Edinb.* **38**, pt. 1 (1917–18).
(4) Robertson, D. *J. Horolog.* (July 1929).
(5) Bloxam, J. M. *Mem. roy. Astr. Soc.* **22**, (1853).
(6) Grossmann, J. and Grossmann, H. *Horlogerie Théorique*, **2**, 194, 415 (1912).
(7) Gebelein, H. *Ingen. Arch.* **6**, pt. 2 (1935).
(8) Atkinson, E. C. *Proc. phys. Soc.* **42**, pt. 2 (Feb. 1930).
(9) Atkinson, E. C. p. 606 of this volume.

DISCUSSION OF THE PRECEDING TWO PAPERS

Sir C. V. Boys wished that the author, who made his own instruments with beautiful workmanship, could work 50 ft. below ground so as to obtain a steady temperature without stratification. A thermostat could never be completely effective because it can only act when a slight change of temperature occurs and the parts of the pendulum take some time to adjust themselves to the slight change; moreover stratification results. At Greenwich it would be possible to drive a hole under the hill and above the river-level without disturbing the transit instruments, but the author lived on clay soil so that he could not conveniently construct an underground laboratory.

Dr G. A. Tomlinson. The experimental results given in table 2 appear to me to prove that the mathematical correction applied on account of the impulse deviation is justified. This correction is a large one and amounts to more than twice the observed changes of rate. The author defines amplitude as the maximum inclination of the pendulum to its free rest position, and the elastic energy of the suspension is therefore strictly proportional to amplitude. The suspension should thus introduce no appreciable deviation from isochronism, leaving only impulse and circular deviations as possible causes of change of rate of the first order. The close agreement with the theoretical values of circular deviation, after a theoretical allowance $86{,}400\,\delta \cot \tau\, 2\pi f$ for the impulse deviation, is an experimental demonstration of the validity of this expression as applied to this particular system of impulsing.

The close agreement the author has obtained in such short trials as these, lasting 4 days in certain cases, suggests that he has an efficient way of comparing the clock

with the rhythmic signals, and I should be pleased to learn what method of observation he uses.

Prof. POLLARD. Recently I have endeavoured to determine the shape and curvature of knife-edges and in the course of devising methods I have obtained some information which might interest Dr Schuler and Mr Atkinson. I have naturally tried out the methods with the finest agate balance edges I could obtain and have found that they all, with the exception of one particularly fine microbalance agate, contact with an optical flat at one or at the most two portions of their whole length. This can easily be seen under the microscope by the system of interference fringes formed in the neighbourhood of the edge.

The cylindric surface of the edge is fortuitously formed by the meet of two facets and if this fortuitous surface is to touch a plane along its whole length obviously the facets must be true planes. The facets of all the agates considerably deviate from plane surfaces, except those of the microbalance agate. In this agate the facets, 8 mm. long and averaging 0·02 mm. wide, approximate to optical flats and consequently the cylindric edge touches an optical-flat along its whole length. The contact, however, is localized along the cylindric surface at numerous short lengths separated by fractures and other imperfections. The ratio of the contacting length to the whole length is important in so far as the permissible loading is concerned. But the measurement of this would be very tedious since a magnification of at least 360 diameters is necessary to observe the minute fringe system in monochromatic light. If a cylindrical planoconvex lens of radius 0·068 mm. is placed perpendicular to the edge of this agate and nearly touching it, the ratio of the principal axes of the elliptic fringe pattern indicates that the radius of curvature is about 3μ., and from the regularity of the fringe pattern with an optical flat it might be supposed that the cylindric surface does not differ very much from that of a circular cylinder. I find that by tilting the optical flat at a small angle to the length of the edge the fringe pattern can easily be seen under the microscope, but I have not had an opportunity of photographing it and obtaining the true shape of the edge by geometrical projection. Some edges that I have examined by these methods are so imperfect that it is difficult to imagine how they would roll on a plane surface.

When the edge is loaded in contact with its bearing, both surfaces will deform into a common surface the shape and breadth of which will depend upon the elastic constants as well as the load, but the limiting load before permanent deformation takes place depends upon the Hertzian hardness. Since agate is crypto-crystalline it is probable that the Hertzian hardness rather than the elastic constants will vary over the common surface; it will certainly vary when the material is steel unless extraordinary precautions are taken in the hardening processes. The common surface will be complex especially in the neighbourhood of the fractures in the case of agate, and in the case of steel it may be permanently deformed locally if the loading is too high. It is evident then that the permissible loading for a knife-edge depends upon the Hertzian hardness, and a method of measuring this for non-brittle materials is described in a paper which I am endeavouring to publish. Presumably

a steel edge will cold-work with use into an unalterable surface condition with greatly increased Hertzian hardness and this may be the explanation of the resistance to wear observed by Gräfe. The super-hardening of steel by cold work is well known and has been applied by E. G. Herbert* in his cloud-burst treatment of steel. As far as I am aware the correct design of a knife-edge bearing has never been fully considered.

The fixing of the knife-edge to the pendulum requires as much care as its construction if the bending referred to by Mr Atkinson is to be avoided. The knife-edge is usually in the form of a triangular prism and is generally force-fitted into a dove-tail groove. The prism is thus held in position by the indeterminate contact of ordinary engineering functional surfaces and is more likely than not to be subjected to unknown bending moments.

The correct way to fix the prism is to work its base as well as the mating surface on the pendulum to optical flatness. The prism can then be wrung into position on the mating surface with the assurance that all parts of the two surfaces are in contact. The prism may be retained in position in a state of repose by four screws which abut normally upon the sloping surfaces in pairs directly opposite one another. With these precautions the prism cannot be subjected to bending moments, provided no part of it overhangs and the plane of pressure never passes outside its base when the pendulum swings through its maximum amplitude.

Prof. Max Schuler (communicated). In the note added February 7, 1936 the author mentions my experiments upon the dependence of the rate on the amplitude of pendulums supported on knife-edges. He has rightly insisted that my experiments show the necessity for distinguishing carefully between the material and the ideal knife-edges. The relation between amplitude and rate is different in the two cases. The ideal knife-edge is a mathematical line, and in this case amplitude deviation is circular deviation. The material knife-edge, on the other hand, is a cylinder of very small radius of curvature rolling on a plane. As this radius, obtained by grinding, has no constant value, amplitude deviation can be determined only by experiment. The shape of the edge can be approximately calculated from the observed deviation.

In my opinion the best edge is not the one which approaches the mathematical line, but that which has the smallest coefficient of friction. A rolling cylinder with a finite radius will reduce undue strain of the materials and consequently permanent deformation and wear are countered. For these reasons I selected for my experiments a knife-edge with very little friction. The logarithmic decrement of the pendulum was only $0{\cdot}127 . 10^{-4}$ per second and this value remained constant between $100'$ and $1'$ of amplitude.

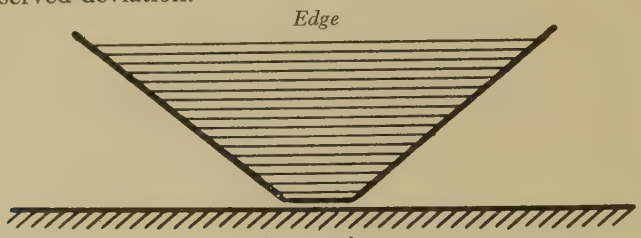
The weight of the pendulum was 8800 g. The case was filled with hydrogen and the pressure was 200 mm. of mercury. The knife-edge is of hardened steel and rests on a polished agate surface. The angle of the knife-edge is 100° and the weight it carries is 4·4 kg. per cm. With this knife-edge the amplitude deviation

* *Trans. Amer. Soc. for Steel Treating*, **14**, 680 (1928).

was quite different from the circular deviation. From this it follows that the edge is not quite sharp but somewhat flattened, as shown, very much exaggerated, in the illustration. The author's assumption that the knife-edge was not absolutely straight is wrong.

I purposely selected this flattened knife-edge in order to ascertain whether the amplitude deviation of the rate would change in the course of time through grinding of the surfaces. Gräfe's experiments, however, proved that the amplitude deviation had not changed after the pendulum had been in use for three years. The knife-edge had, therefore, not altered during this period and no effect of wear is yet observable.

Very exact observations of the deviation could be made, for these were taken on the free pendulum with the electrical impulse cut off. I was thus able to eliminate impulse errors which, as the author says, were responsible for by far the largest errors in his measurements. The measurement was accurate to about 1 per cent of the observed deviation.



If the author were to conclude that a pendulum suspended by a spring is better for time-keeping purposes than one supported by a knife-edge, I could not agree with him. The rate should be a single-valued function of the amplitude. This function must not alter in the course of time. That such a function is possible I have proved experimentally. It is not important for the result whether the amplitude deviation equals circular deviation as calculated by the mathematician for the circular pendulum. It is possible to produce knife-edges for which the difference between amplitude deviation and circular deviation is much smaller than with those I have employed. I did not consider this of any importance and I evolved my knife-edge according to my conception of the best form. No other pendulum time-keeper has shown results as good as those obtained with my pendulum supported on a knife-edge. The results of relative gravity measurements with knife-edge-supported pendulums confirm my opinion. For such purposes knife-edge-supported pendulums are to-day used with very accurate results.

My study of the subject leads me to the conclusion that the makers of astronomical standard clocks will, in the near future, employ this knife-edge support exclusively.

Author's reply. Sir Charles Boys naturally wishes the pendulums at Greenwich to enjoy the steady underground temperature which has been secured for the astronomical clocks at Paris. Yet I am not certain that an invariable temperature is the best thing for invar rods. Observations made at Greenwich, Yale and Göttingen under thermostatic control suggest that abrupt changes of rate occur

more readily under these conditions than when pendulum temperature is constantly changing (see also § 16). On the other hand, Shortt 44 in Paris during 1935 was free from changes which could be attributed to invar: such changes as did occur were purely erratic.

Dr Tomlinson is not justified in assuming that the suspension "introduces no appreciable deviation from isochronism" until Sampson's equations have been solved without rejecting squares and higher powers of the displacement. The spring complicates matters not only by supplementing the restoring couple due to gravity but also by modifying the path of the centre of gravity of the pendulum. Dr Tomlinson has surely overlooked air resistance and air inertia as possible causes of deviation when he speaks of impulse and circular deviation as the only causes left for change of rate. If all the matters referred to in § 2 could be decided without recourse to experiment, I should agree that my experiment would be simply a test of the correctness of the formula for impulse deviation.

During the 5 minutes' transmission of rhythmic signals there are five coincidences. I attempt to estimate to the nearest half-second and when in doubt I avail myself of all the coincidences. Precision is reduced by atmospherics and other disturbing noises and is increased by the cleanness and brevity of the two signals. In the early days of the Rugby transmission the Greenwich dots were far too long and inferior in this respect to the Paris signals. There has been improvement, but still shorter signals are much to be desired.

My earliest apparatus had a low-resistance earpiece for the clock signal and a high-resistance one for the wireless signal. The latter sounded in the left ear, but one day the phones were accidentally reversed so that the left ear, accustomed to a signal overtaking the other before coincidence, found itself listening to a signal ahead of the other. I could not avoid concluding that the coincidence was already past and was quite unable to make an observation.

Prof. Pollard's studies of knife-edges are of great interest. The optical method gives a measure of the mean radius of curvature, whilst the pendulum deviation indicates how this varies from point to point. I hope that Prof. Pollard will soon be able to determine the form of the edge. The elastic deformation, due to loading, probably modifies the pendulum deviation to an appreciable extent. Both Gebelein and I assume the edge and the supporting surface to be rigid, so the results must be regarded as first approximations. I conclude that a pendulum with a good knife-edge correctly attached is at present a rarity. The attaching of a good suspension spring is not a formidable task, but the making of it is another matter. I hope some day to accomplish this with more certainty than at present.

Dr Schuler is in favour of using knife-edges for supporting pendulums, believing that better timekeeping is secured in this way than with suspension springs. Gräfe's observations indicate good rate-holding quality for an edge, but I have not yet seen records of timekeeping with the Schuler pendulum which encourage the expectation that the knife-edge will replace the suspension spring. In a future paper I hope to describe experiments dealing with the capacity of different pendulums to maintain a constant rate.

535·342

ABSORPTION SPECTRA AND PHOTODISSOCIATION OF SOME INORGANIC MOLECULES

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ABSTRACT. The absorption spectra of PCl_3, PBr_3, PCl_5, PBr_5, $POCl_3$, P_2O_5, $AsCl_3$, $SbCl_3$, SbOCl, and $BiCl_3$, are investigated. The regions of selective absorption are correlated to certain photodissociation processes. A comparison with the mean bond energies as known from thermochemical measurements, allows certain conclusions to be drawn as to the structure of these molecules.

§ 1. INTRODUCTION

Continuous absorption spectra of polyatomic molecules have been investigated recently by a number of authors. The following work was undertaken in order to supplement the results obtained by Butkow[1] and Trivedi[2] for molecules formed by the fifth-group atoms P, As, Sb, and Bi, and so derive some general rules about the photodissociation of more complex inorganic molecules. The spectra of SbI_3, $BiBr_3$, and BiI_3 as measured by Butkow show a definite structure and several maxima in each case, whereas Trivedi has found a long-wave limit only. This difference leads to a fundamental difficulty which must be discussed at the outset. A continuous absorption spectrum means a process of photodissociation, i.e. a transition from the stable ground state of the molecule to a repulsive curve in the Franck-Condon diagram. A comparison of the long-wave limit with bond energies calculated from thermochemical measurements is possible, however, only if this long-wave limit really represents the transition to the repulsive curve from the vibrationless ground state. As soon as the population of the higher vibrational levels of the ground state is increased so that these higher levels influence the absorption spectrum, the long-wave limit shifts towards longer wave-lengths, because the energy difference between the higher levels and the repulsive curve is smaller. This effect is the more marked, the steeper the slope of the repulsive curve. In fact, by increasing the population of the higher vibrational terms, either by increasing the absolute number of molecules under investigation by longer absorption tubes or by increasing the percentage of molecules with excited vibrational levels by increasing the temperature of the gas or vapour, it is experimentally possible to shift the long-wave limit towards longer wave-lengths inside very wide limits. The original investigations of Franck and his collaborators were concerned with the alkali halides in which the repulsive curve is rather flat owing to Van der Waals forces between the non-ionized atoms in their respective ground

ates, and the agreement between the optical and thermochemical measurements as very good. Subsequently this feature of the continuous absorption spectra has been sometimes overlooked. This has led to some attempts to prove the ionic nature of the bonds of the hydro-halides in the gaseous state by shifting the long-wave limit to smaller energy values, whereas the Raman effect, the electric conductivity and the dipole moment establish the bond as that of a covalent dipole molecule[3]; or, in cases like methyl iodide, where the absorption spectrum yields a value far above the thermochemical one on account of the steepness of the repulsive curve, attempts have been made to diminish the optical value, again by shifting the long-wave limit artificially towards smaller energy values[4]. We think such attempts are misleading, since only the transition from the vibrationless ground state of the molecule has a good physical meaning for comparison with thermochemical bond energies. There remains, however, the difficulty of deciding which of the many possible values of the long-wave limit corresponds to this transition. According to the Beer-Lambert law the absorption of the vibrationless molecule can be represented by a curve connecting wave-length and the number of molecules. Hence, if the number of molecules is not big enough, e.g. if the vapour pressure is too low, the long-wave part of the curve will not be reached at all and the determined energy of the long-wave limit will be far too high. If, on the other hand, the number of molecules is too big, the number of molecules in higher vibrational levels is also increased, and the measured energy of the long-wave limit is far too low (cf. figures 2 to 5). The decision is easier if the continuous absorption spectrum shows in the region investigated a structure, which indicates definitely the part of the absorption curve really measured. The greater the excitation of higher vibrational levels, the more broadened the absorption regions become. As can be seen from the Franck-Condon curve, transitions from higher levels and bigger internuclear distance broaden each maximum towards longer wave-lengths, those from the same levels and smaller internuclear distance produce the same effect towards shorter wave-lengths. The different regions of selective absorption, therefore, ultimately merge into one continuous spectrum without any structure. Consequently the value of the long-wave limit in a spectrum still showing distinct maxima and minima will be nearer to the true value for the vibrationless molecule. Wherever possible, i.e. wherever the maxima appear in the region investigated, only such values should be taken into account. Accordingly we have measured the absorption spectra of several molecules, formed by atoms of the fifth group, including some for which only the long-wave limit was determined by previous workers. The spectra of the following substances have been taken: PCl_3, PBr_3, PCl_5, PBr_5, $POCl_3$, P_2O_5, $AsCl_3$, $SbCl_3$, SbOCl, and $BiCl_3$.

§ 2. EXPERIMENTAL

As absorption cells, tubes of fused silica of 5, 10 and 20 cm. long, connected with the usual vacuum arrangement and manometer, were used. In the case of liquids the substances were contained in a side bulb and the vapour introduced in the apparatus after repeated evacuation and thorough washing of the absorption

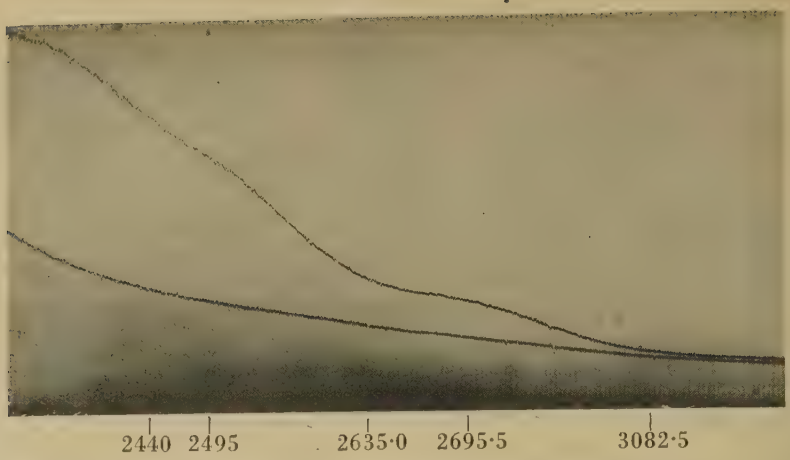

Figure 1. Upper curve = absorption of PBr_3, absorption cell 1 cm. length, vapour pressure = 4 mm
Lower curve = source of light.

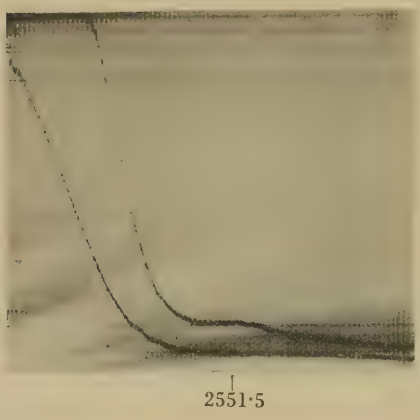

Figure 2. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm. length, 61° C. Lower curve = source of light.

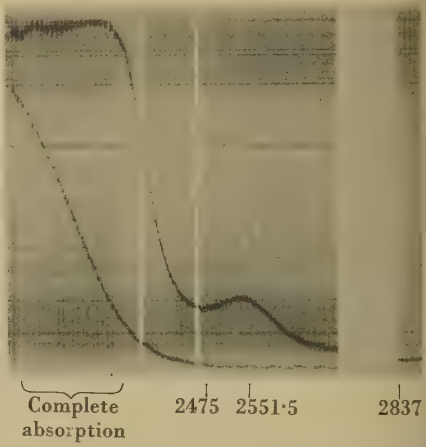

Figure 3. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm., length, 72° C. Lower curve = source of light.

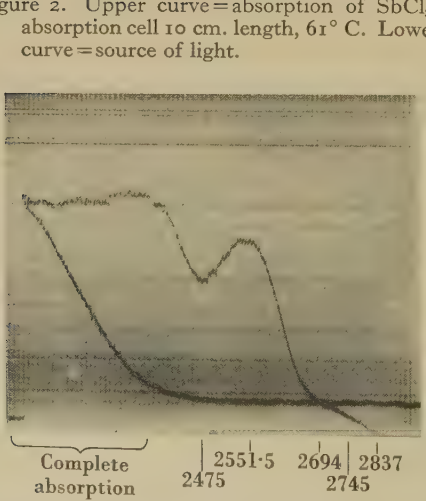

Figure 4. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm., length, 84° C. Lower curve = source of light.

Figure 5. Upper curve = absorption of $SbCl_3$, absorption cell 10 cm., length, 130° C. Lower curve = source of light.

ell by the vapour itself. During longer exposures the vapour was frequently re-ewed. Solids were introduced in the absorption cell itself in small quantities and he cell heated either by an electric stove or, if there was danger of decomposition, y a current of warm air. The H_2 continuous spectrum was used as a source, Cu rc lines as standards, and the Hilger medium quartz spectrograph as the resolving nstrument. The density of the spectra was measured on the recording microphoto-neter, the long-wave limits and the positions of the absorption maxima were deter-nined from the photometer plates, of which figures 1 to 5 are typical.

Phosphorus tribromide. The spectrum of PBr_3 at 4 and 5 mm. vapour pressures n a 5 cm. tube shows complete absorption to about λ 3200 and λ 2450 respectively, nd at 4 mm. pressure in a 1 cm. tube, to λ 2360. The photometer plate of the latter hows two flat maxima at λ 2695·5, ν 37088 and λ 2495, ν 40068 (see figure 1), with n energy difference of 0·37 V. The corresponding long-wave limits are λ 3082·5, 32432 and λ 2635·0, ν 37939 respectively; the third long-wave limit (following he second maximum) is not very well defined but lies at about λ 2440, ν 40971. Thus the absorption due to the first maximum covers a region of about 5500 $cm.^{-1}$, hat due to the second about 2000 $cm.^{-1}$ only. Hence the first (lower) of the two epulsive curves is the steeper, and the energy difference between them will be lightly less than the real difference between the separated systems. Since the term ifference $^2P_{\frac{1}{2}}$–$^2P_{\frac{3}{2}}$ of the Br atom is 3685 $cm.^{-1}$ or 0·38 V., i.e. slightly greater than hat between the two maxima, the two dissociation processes are probably

$$PBr_3 \rightarrow PBr_2 + Br(^2P_{\frac{3}{2}})$$

nd

$$PBr_3 \rightarrow PBr_2 + Br(^2P_{\frac{1}{2}}).$$

The third region at shorter wave-length will probably have an excited $—PBr_2$ adical as one of its products. The first long-wave limit λ 3082·5 gives 92·0 kcal./mol. or the photodissociation of PBr_3 in its ground state; the values of the other two ong-wave limits are 108·1 and 116·2 kcal./mol. respectively.

Phosphorus trichloride. The continuous absorption of PCl_3 is slightly less liable o changes with increase of pressure; this may be due to an increased spacing of he vibrational levels of the ground state. The beginnings of complete absorption in c. 10 cm. tube are roughly as follows:

Pressure (mm.):	3·5	8	18	40	60
λ (A.):	2410	2440	2460	2490	2520

No maxima could be observed on the photometer plates, probably because they are t shorter wave-lengths than in PBr_3. Trivedi[2] obtained λ 2957 as the long-wave imit (tube-length and pressure not mentioned, probably high) while the micro-photogram of the second of the above spectra revealed a value of λ 2815·5, ν 35507 or 101·2 kcal./mol.

Phosphorus pentabromide. The spectrum of PBr_5 shows Br_2 absorption bands learly at 55° C. and fully developed at 72° C.; lower temperatures and corre-ponding vapour pressures had, therefore, to be used. With 4 mm. pressure and a 0 cm. cell the spectrum shows a maximum at λ 2744, ν 36432, and retransmission

occurs at λ 2688, ν 37191 or 105·1 kcal./mol.; the first long-wave limit is λ 3146 ν 31777 or 99·0 kcal./mol. The extent of this first region of selective absorption indicates again a steep repulsive curve. A correlation of the two regions of absorption with particular processes of photodissociation is not possible, since the second maximum could not be determined and the energy difference of the long-wave limits themselves depends too much on experimental conditions to be used with safety.

Phosphorus pentachloride. The spectrum of PCl_5 indicates decomposition (Cl absorption) at about 80° C. upwards. At about 25° C. (room temperature) and 6 mm. pressure complete absorption occurs from λ 2130 onwards. The plates chosen for final measurement were taken up to 55° C. and 10 mm., under which conditions the absorption spectrum seems fully developed. As in the case of PBr_5 one single maximum was obtained at λ 2310, ν 43277; the two long-wave limits are λ 2240, ν 44629 or 126·7 kcal./mol. and λ 2625, ν 38084 or 108·1 kcal./mol. The extent of about 6500 $cm.^{-1}$ indicates again a steep repulsive curve.

Phosphorus pentoxide shows a spectrum with continuous end-absorption only; no maximum was found. At 450° C. in a 10 cm. cell the absorption is complete from λ 2200 onwards, and at 563° C. (the melting point) from λ 2400. The corresponding long-wave limits are λ 2270, ν 44039 or 124·9 kcal./mol. and λ 2530; ν 39514 or 112·0 kcal./mol. respectively.

Phosphorus oxychloride. The spectrum of $POCl_3$ at 3·5 cm. vapour pressure in a 20 cm. cell shows complete absorption from λ 2200, and a long-wave limit at λ 2250, ν 44431 or 126·0 kcal./mol. With reduced pressure no maximum could be detected on a Schumann plate down to about λ 1900.

Arsenic trichloride. Complete absorption obtains in $AsCl_3$ at about 25° C. in a 10 cm. cell from about λ 2390 onwards at 2 mm. vapour pressure, about λ 2420 at 6 mm. and about λ 2510 at 12 mm. Photometric measurements of the first of these spectra show one maximum at λ 2547, ν 39250; the preceding and following long-wave limits lie at λ 2687, ν 37205 or 105·6 kcal./mol. and λ 2475, ν 40392 or 114·8 kcal./mol. Trivedi[2] obtained a long-wave limit at λ 3466 or 82·1 kcal./mol., but no structure of the spectrum; we therefore believe our value to be the more accurate for the vibrationless molecule. According to the extent of the first region of absorption the repulsive curve seems to be again rather steep.

In $AsCl_3$, and in $SbCl_3$ and $BiCl_3$ (below), a correlation of the different regions to particular photodissociation processes is not possible at the present moment, since the Cl atom does not possess any low terms (besides the very small ^2P separation which cannot be recognized in such spectra) and those of the respective radicals are not yet known.

Antimony trichloride. The change of absorption with temperature and pressure can be seen from the following figures for the beginning of complete absorption in a 10 cm. cell:

Temperature (°C.):	25	61	72	84	130
Pressure (mm.):	0·5	2	2·5	3	12
λ (A.):	2190	2305	2350	2410	2620

The micro-photograms show a flat maximum at λ 2745, ν 36419, and a second very high and prominent maximum at λ 2551·5, ν 39181. The long-wave limits of the three regions of absorption are λ 2837, ν 35238 or 99·8 kcal./mol., λ 2694, ν 37109 or 105·3 kcal./mol., and λ 2475, ν 40392 or 114·8 kcal./mol. Trivedi[2] found λ 3256 or 87·3 kcal./mol. as the first long-wave limit, but no structure of the spectrum; our value appears to be the more accurate for the vibrationless molecule. According to the extents of the different regions of selective absorption the first repulsive curve is less steep, but the second one even slightly less steep as in $AsCl_3$.

Antimony oxychloride. Since this substance seems liable to decomposition when heated its spectrum is difficult to obtain. At 100° C. in a 10 cm. cell the long-wave limit was found at λ 2460, ν 40638 or 115·2 kcal./mol.; this energy may be still slightly too high on account of insufficient vapour pressure (about 4 mm.). No structure was observed.

Bismuth trichloride. The absorption by $BiCl_3$ in a 10 cm. absorption cell is complete from λ 2200 onwards at 90° C., from λ 2240 at 160° C., from λ 2370 at 240° C., from λ 3340 at 290° C., and from λ 4100 at 335° C. It shows a marked maximum at λ 2800, ν 35704, and the long-wave limits of the two regions of selective absorption lie at λ 3350, ν 29842 or 83·6 kcal./mol., and λ 2660, ν 37583 or 106·7 kcal./mol. The first repulsive curve appears to be rather steep. Trivedi[2] found the first long-wave limit at λ 3656 or 77·2 kcal./mol., but no structure; our value therefore seems to be the more accurate for the vibrationless molecule.

§ 3. THERMOCHEMICAL CALCULATIONS

In order to know more about the processes of photodissociation, we have to compare the energies so determined with the atomic energies of dissociation (D) of the molecules in question. Following Born and Haber's cycle we calculate this energy by adding to the heat of formation from the elements (Q) the energy necessary to convert the elements into gaseous atoms and (if Q refers to the liquid or solid state) deduct the heat of vaporization or sublimation of the compound. The energy necessary to transform a solid or liquid non-metallic element into its atoms in the gaseous state comprises the energy of sublimation (S) or of vaporization (L) alone, the energy of dissociation of the diatomic molecule (D), and, sometimes the energy necessary to split up a polymerized molecule like S_8 into diatomic molecules. Of these different energies S and L are more or less known for the elements, but only few measurements are available for the compounds. These quantities are small, however, compared with Q and D and may therefore be estimated by one of the known empirical rules; we have mostly used Walden's rule[5] for L and Forcrand's rule[6] for S; if T_m and T_b denote the melting and boiling points respectively (absolute temperatures), we have $L \div 13{\cdot}5\ T_m$ and $S \div 30\ T_b$. The heat of formation Q is mostly accurately measured. The energies of dissociation of the diatomic elements are determined spectroscopically; they can be determined with extreme accuracy, if a point of convergence is measured in the band spectrum and the products of dissociation are known; if, however, the

latter are doubtful, or if D is determined by linear extrapolation of the vibrational levels, the results are liable to later corrections. In the following we shall use other authors' results on the absorption spectra of polyatomic molecules in the vapour state, but a number of recent corrections of the dissociation energies of the diatomic molecules render necessary a recalculation of all the older data. The elements of interest for the following comparison are the halogens, nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur, and tellurium.

The spectra of the halogens show a convergence point; the dissociation products are an unexcited and an excited $^2P_{\frac{1}{2}}$ halogen atom; from these considerations D has been determined to be 56·9, 45·2, and 35·6 kcal./mol. for Cl_2, Br_2, and I_2 respectively[7]. For N_2, whose dissociation energy had been calculated to 207·5 kcal./mol. by linear extrapolation of the vibrational levels, a new value, $D = 169$ kcal./mol., taken from predissociation is now available[8]. The dissociation energy of P_2 has been determined from its predissociation as 115·5 kcal./mol. or 5·008 V.[9] For As_2, Sb_2, and Bi_2 no values are available; we have therefore estimated their dissociation energies as roughly 4, 3, and 2 V., using certain empirical rules obtained from band spectrum data[10]; these values, though not accurate, are believed to give the correct order of magnitude. In O_2 a convergence point is directly measured, but from its energy value the ^1D term value of O has to be deducted, giving $D = 117{\cdot}4$ kcal./mol.[11] The predissociation of S_2 yields a value $D = 102{\cdot}6$ kcal./mol. Rosen[12], who observed directly the convergence points in the spectra of S_2, Se_2, and Te_2 as 4·94, 3·81, and 3·22 V. respectively, believed the dissociation products to be an unexcited S atom and a S atom in a higher component of the ^3P ground state. Later investigation of the S_2 and Se_2 spectra have made it clear, however, that this analogy with the halogens is not correct; rather, as in O_2, the dissociation products of the upper $^3\Sigma$ level are $S(^3P) + S(^1D)$ etc. and hence the ^1D term value has to be deducted from the convergence point. Since these term values have recently been determined[13] as 1·14, 1·18, and 1·30 V. for S, Se, and Te respectively, new and more accurate values for the dissociation energies may be obtained in this way[14], namely 3·80 V. or 88·4 kcal./mol. for S_2, 2·63 V. or 59·3 kcal./mol. for Se_2, and 1·92 V. or 43·7 kcal./mol. for Te_2.

The definite values to convert elements which appear in thermochemical equations as solids or liquids, are obtained from the above dissociation energies by adding S or L respectively and, where necessary, the energy of polymerization. Phosphorus may serve as an example:*

$$[P] \rightarrow (P_4) = 18 \text{ kcal./gm. atom (M)}$$
$$(P_4) \rightarrow 2(P_2) = 30 \text{ kcal./gm. atom (M)}$$
$$(P_2) \rightarrow 2(P) = 58 \text{ kcal./gm. atom}$$
$$\overline{[P] \rightarrow (P) = 106 \text{ kcal./gm. atom}}$$

* Here and in table 1 data taken from J. W. Mellor's *Comprehensive Treatise* and from Landolt and Boernstein's tables are marked by (M) and (LB) respectively. (W) and (F) denote estimates by means of Walden and Forcrand's rules respectively. [ ] stands for the solid, ( ) for the gaseous state, no bracket marks the liquid state.

The values used here are 25 kcal./gm. atom for Br, 21 for I, 106 for P, 104 for As, 95 for Sb, 68 for Bi, 59 for S, and 48 for Te; they are not all of equal accuracy, some of them comprising estimated values. For the gaseous elements N_2, Cl_2, O_2 half of the optical energies of dissociation is used. The results are given in table 1.

§ 4. DISSOCIATION PROCESSES AND BOND ENERGIES

In order to correlate the energies of photolytic decomposition, as measured by the continuous absorption spectrum, to particular processes of photodissociation, we have to compare them with the bond energies of the molecules in question. For this purpose we divide the energies of dissociation into constant parts, corresponding to particular bonds. Thus from $\frac{1}{3}D(PCl_3)$ we get the energy of the P—Cl bond as 87 kcal./mol. It should be clearly understood that these values, which we shall call the "*mean bond-energy*" D_B, are not identical with the true energies of the bonds in question. On the contrary, on account of the repulsive forces between the atoms in the formation of this molecule the first Cl atom of PCl_3 is probably linked to P with a greater amount of energy than the second and third Cl, i.e. $D(P+Cl) > D(PCl+Cl) > D(PCl_2+Cl)$. Since the process of photodissociation begins with the completed molecule, the mean bond energies will be upper limits.

It can be seen, however, that an approximate additivity exists, since it is possible to represent, e.g., the energy of dissociation of the oxychlorides as the approximate sum of the mean bond energies derived from the chlorides and oxides. Thus, for example,

$$D(PCl_3)=261; \quad D_B(P^{III}—Cl)=87.$$
$$D(PCl_5)=343; \quad D_B(P^{V}—Cl)=69.$$
$$D(P_2O_5)=833; \quad D_B(P^{V}=O)=167.$$
$$3D_B(P^{V}—Cl)+D_B(P^{V}=O)=374; \quad D(POCl_3)=386.$$

Again,
$$D(SbCl_5)=331; \quad D_B(Sb^{V}—Cl)=66.$$
$$D(SbCl_3)=262; \quad D_B(Sb^{III}—Cl)=87.$$
$$D(Sb_2O_3)=502; \quad D_B(Sb^{III}=O)=167.$$
$$D_B(Sb^{III}=O)+D_B(Sb^{III}—Cl)=254; \quad D(SbOCl)=260.$$

In organic chemistry an approximate additivity of the mean bond energies has been known for a long time and used in all calculations based on the heats of combustion; in inorganic chemistry, however, this does not appear to have attracted much attention as yet. Considering the uncertainty and inaccuracy of many of the figures used, the agreement between the calculated and observed figures is quite satisfactory. Among the chlorides and oxychlorides of sulphur, similar calculations are possible, but are more difficult because the energy of formation of gaseous SCl_2 is not known. Asundi and Samuel[14] have shown, however, that the bond energies of the derivatives of di- and tetravalent sulphur remain approximately constant, if the results of optical measurements are used.

Table 1

Molecule	Equation	L	S	D	Observed long-wave limit λ (A.)	kcal./mol.	Ref.	Notes
(PBr_3)	$[P]+\frac{3}{2}Br_2=PBr_3$ + 42·6 (M)	3 (W)		218				
(PCl_3)	$[P]+\frac{3}{2}(Cl_2)=(PCl_3)$ + 69·7 (LB)			261				
(PBr_5)	$[P]+\frac{5}{2}Br_2=[PBr_5]$ + 63·5 (M)		11 (F)	280				
(PCl_5)	$[P]+\frac{5}{2}(Cl_2)=[PCl_5]$ +107 (LB)		12 (F)	343				
(P_2O_5)	$2[P]+\frac{5}{2}(O_2)=[P_2O_5]$ +358 (LB)		30 (F)	833				
($POCl_3$)	$[P]+\frac{1}{2}(O_2)+\frac{3}{2}(Cl_2)=POCl_3$ +145 (LB)	9 (LB)		386				
($AsCl_3$)	$[As]+\frac{3}{2}(Cl_2)=AsCl_3$ + 74·7 (LB)	7 (M)		257				
($SbCl_3$)	$[Sb]+\frac{3}{2}(Cl_2)=[SbCl_3]$ + 91·4 (LB)		10 (F)	262				
(SbOCl)	$[Sb]+\frac{1}{2}(O_2)+\frac{1}{2}(Cl_2)=[SbOCl]$ + 89·8 (M)		12 (F)	260				
($BiCl_3$)	$[Bi]+\frac{3}{2}(Cl_2)=[BiCl_3]$ + 91 (LB)		18 (M)	226				
(PI_3)	$[P]+\frac{3}{2}[I_2]=[PI_3]$ + 10·9 (LB)		10 (F)	169	3147	90·4	(2)	(*a*)
($AsBr_3$)	$[As]+\frac{3}{2}Br_2=[AsBr_3]$ + 45·5 (LB)		14 (F)	208	3248	87·6	(2)	(*a*)
(AsI_3)	$[As]+\frac{3}{2}[I_2]=[AsI_3]$ + 13·5 (LB)		12 (F)	168	5616	50·6	(2)	(*a*)
($SbBr_3$)	$[Sb]+\frac{3}{2}Br_2=[SbBr_3]$ + 61·4 (LB)		11 (F)	220	5450	52·2	(2)	(*a*)
($SbCl_5$)	$[SbCl_3]+(Cl_2)=SbCl_5$ + 13·8 (M)		11 (LB)	331	4130	68·9	(2)	(*a*)
(SbI_3)	$[Sb]+\frac{3}{2}[I_2]=[SbI_3]$ + 28·8		13 (F)	173	4150	68·3	(1)	(*b*)
(N_2O_5)	$(N_2)+\frac{5}{2}(O_2)=(N_2O_5)$ − 1·2			451·8	2800	101	(16)	(*c*)
(Cl_2O)	$(Cl_2)+\frac{1}{2}(O_2)=(Cl_2O)$ − 23			93	6665	45·5	(17)	(*d*)
(SO_3)	$[S]+\frac{3}{2}(O_2)=(SO_3)$ + 91·9 (LB)			327	3300	86·7	(18)	(*e*)
(TeO_3)	$[Te]+\frac{3}{2}(O_2)=[TeO_3]$ + 83·6 (M)		*ca.* 24	284	4600	62·1	(16)	

(*a*) Trivedi[2] observed no structure such as is observed by Butkow and ourselves; the vapour pressure was too high. His energy values are therefore too small; the correct values for the vibrationless molecule will probably be 10 to 20 per cent higher.

(*b*) Butkow[1] also investigated BiI_3 and $BiBr_3$, but no thermochemical data are available for these substances.

(*c*) Urey, Dawsey and Rice[15] observed a long-wave limit at λ 3050. Dutta and Sen Gupta[16] observed two regions of absorption, one with a long-wave limit at λ 2800 and another extending from about λ 4500 to λ 3200. This continuum, as may be seen in the published spectra, appears in the middle of the NO_2 band system (also present) and is solely due to NO_2. Any system of absorption bands can be made to appear as a pseudo-continuous spectrum if the vapour pressure, and therefore the population of the higher vibrational levels, is high enough, until for the liquid state only the envelope of the system remains as continuous absorption. As can be seen from a Franck-Condon diagram, the overlapping will always begin in the middle of the system and spread towards longer and shorter wave-lengths. The new bands at shorter wave-lengths are due to transitions from higher vibrational levels of the ground state at small internuclear distances, those at longer wave-lengths to the same transitions at larger internuclear distances. We shall therefore ignore this first absorption and accept as the real absorption of N_2O_5 their value of λ 2800 or 101 kcal./mol., this being slightly the higher value.

(*d*) This long-wave limit is due to the dissociation process $Cl_2O \rightarrow ClO + Cl$; various maxima indicate further processes of photodissociation into unexcited and excited products.

(*e*) The first absorption maximum observed by Dutta[18] has a long-wave limit at λ 3300. The second absorption region is correlated to the process $SO_3 \rightarrow SO_2 + O(^1D)$. The absorption spectra of SCl_2, $SOCl_2$, S_2Cl_2, and SO_2Cl_2 have recently been measured by Asundi and Samuel[14]. For the calculation of the atomic heat of formation a rough value of 90 kcal./mol. was used for $D(S_2)$, instead of 88. With this correction the energies of dissociation are: $D(SCl_2)=125$, $D(SOCl_2)=214$, $D(S_2Cl_2)=181$, and $D(SO_2Cl_2)=216$. The value of $D(SCl_2)$ [illegible]

The above figures show that the rule of additivity obtains only so long as the central atom does not change its state of valency. It is, for instance, not possible to represent the dissociation energy of $POCl_3$ if the value of $D_B(P^{III}—Cl)$ is employed, or that of SbOCl by means of $D_B(Sb^{V}—Cl)$. Furthermore, the mean bond energy of a lower state of valency is always bigger than that of a higher one. The bond energies of di- and tetravalent sulphur derivatives remain, however, apparently constant. This clearly indicates that the difference of the mean bond energies is produced by the activation of the helium-like repulsive group of electrons, which remains an s^2 group with respect to the central atom in PCl_3, SCl_2, $SOCl_2$, and therefore must have undergone fission, i.e. must have been transferred to an sp or p^2 group, in $POCl_3$, SO_2Cl_2, etc., causing a rearrangement of the electronic configuration of the molecule. Exactly the same behaviour is well known from molecular refractivity and parachor[19]. This is not astonishing, since any molecular quantity which follows approximately the law of additivity may be subdivided in two different ways: either by introducing additive constants for the various atoms or for the various bonds. But each kind of division will always retain some of the features of the other kind.

Besides the mean bond energies there exists, however, a second set of figures, which we have to take into account for the sake of comparison. For derivatives of penta- and hexavalent atoms the energies of certain dissociation processes are independently known, either by direct measurements or as the difference of two atomic heats of formation. Thus, by adding $\frac{1}{2}D(O_2)=58{\cdot}7$ to the equation

$$(SO_2)+\tfrac{1}{2}(O_2)=(SO_3)+23{\cdot}5,$$

we obtain about 82 kcal./mol. for the process of dissociation $(SO)_3 \rightarrow (SO_2)+(O)$; if we add $D(SO_2)=247$ to this, we obtain $D(SO_3)=329$ kcal./mol., whereas calculation from the elements gives 327 kcal./mol. Such values, directly determined by thermochemical experiments, we shall denote by D_T. They are, of course, entirely different from bond energies, which measure the *adiabatic* dissociation of a molecule. Thus the diamagnetic molecule SO_3 is certainly not formed by the chemical union of unexcited SO_2 and unexcited O atoms. The ground level of O is the paramagnetic ^3P term, whereas SO_2 possesses a diamagnetic ground level and their combination does not allow for a diamagnetic ground level of SO_3. Of the products of adiabatic dissociation of SO_3 into SO_2+O, therefore, at least one is excited, i.e. in an energy diagram, the curve of *adiabatic* dissociation connects the ground state with the level of excited atoms or radicals. D_T, on the other hand, measures the difference of the energy contents of the two systems SO_3 and SO_2+O with respect to the level of the unexcited dissociation products, without regard to the actual adiabatic formation of the molecule. Since all the saturated molecules dealt with here are diamagnetic, and all the atoms in question belong either to the sixth or to the seventh group with paramagnetic ground states, the same is true of all of them. Also, in cases like the dissociation $PCl_5 \rightarrow PCl_3+2Cl$, it is established by the magnetic properties of the molecules and atoms, that at least one of the products of the adiabatic dissociation is excited.

Table 2

Molecule	Dissociation process	Mean bond energy D_B	Thermo-chemical energy D_T	Optical dissociation energy D_0	$D_0 - D_T$	$D_0 - D_B$	Reference
N_2O_5	O_2—N—O—NO + O	90·2	—	101	—	11	(15)
	$2NO_2 + O$	—	63·8	101	37	—	(16)
PCl_3	$PCl_2 + Cl$	87	—	101	14	—	Present paper and (2)
PBr_3	$PBr_2 + Br$	73	—	92	19	—	Present paper
PI_3	$PI_2 + I$	56	—	87	31	—	(2)
PCl_5	$PCl_4 + Cl$	69	—	108	39	—	Present paper
	or $PCl_3 + 2Cl$	—	75	108	—	33	
PBr_5	$PBr_3 + Br$	58	—	90	32	—	
	or $PBr_2 + 2Br$	—	60	90	—	30	,, ,,
$POCl_3$	$POCl_2 + Cl$	69	—	127	58	—	
	or $PCl_3 + O$	—	125	127	—	2	,, ,,
P_2O_5	$P_2O_4 + O$	167	—	129	−38	—	
	or $\frac{1}{2}P_2O_3 + O$	—	?	129	—	?	,, ,,
$AsCl_3$	$AsCl_2 + Cl$	86	—	106	20	—	Present paper and (2)
$AsBr_3$	$AsBr_2 + Br$	69	—	> 88	> 19	—	(2)
AsI_3	$AsI_2 + I$	56	—	> 51	> − 5	—	(2)
$SbCl_3$	$SbCl_2 + Cl$	87	—	99	12	—	Present paper and (2)
$SbBr_3$	$SbBr_2 + Br$	73	—	> 52	> −21	—	(2)
SbI_3	$SbI_2 + I$	57	—	68	10	—	(1)
SbOCl	$SbO + Cl$	87	—	117	30	—	Present paper
$SbCl_5$	$SbCl_4 + Cl$	66	—	> 69	> 3	—	(2)
	or $SbCl_3 + 2Cl$	—	81	> 69	> −12	—	
$BiCl_3$	$BiCl_2 + Cl$	75	—	85	10	—	Present paper and (2)
Cl_2O	$ClO + Cl$	46·5	43	43	0	−3·5	(17)
SCl_2	$SCl + Cl$	< 60	—	55	< 5	< 5	(14)
SCl_2	$S + 2Cl$	< 120	—	104	> −16	—	(14)
$SOCl_2$	$SO + 2Cl$	96	—	97	1	—	(14)
S_2Cl_2	$S_2 + 2Cl$	93	—	104	11	—	(14)
SO_2Cl_2	$SOCl_2 + O$	—	102	109	—	7	(14)
SO_3	$SO_2 + O$	109	82	87	−22	5	(18)
TeO_3	$TeO_2 + O$	95	53	62	−33	1	(16)

In this connexion it is of interest to note, that the values D_T are always smaller than the corresponding values of D_B. This clearly indicates that the adiabatic dissociation does indeed reach a higher level of the separated system. It seems likely that this is connected with the conception of the s^2 group undergoing fissure in order to lose its repulsive character, since this again involves the excitation of one of the dissociation products.

In table 2 the long-wave limits D_0 of the absorption spectra are compared with the values of D_B and D_T, and it appears as if several general rules can be derived therefrom. We consider first the molecules formed by the trivalent atoms of the fifth group. Here D_0 is always much bigger than D_B. The true bond energy of the halogen split off first will even be less than D_B, and we have therefore to assume that the long-wave limit represents a transition from the ground state of the molecule to a very steep repulsive curve. The width of the first absorption region also points in this direction. Since all these molecules exhibit a covalent linkage, as indicated by their conductivity, low boiling point, dipole moment and Raman effect, Butkow[1] assumes that the products of the first photolytic dissociation are an unexcited radical and an excited halogen atom. This assumption, which is based on Franck's criterion of the ionic or electrovalent linkage[7], cannot be proved directly, since the exact energy of dissociation is not known.

It has been shown, however, that it is not possible to ascribe general validity to Franck's criterion, although it holds good in many simple di- and triatomic molecules. As Herzberg and Franck and his collaborators have shown[21], it cannot be rigorously valid, because intersections of the potential curves of covalent molecules occur, and therefore Franck's criterion is a necessary but insufficient condition of electrovalent linkage. Thus the ground level of a covalent molecule may be formed by the combination of excited atoms; consequently an excited level of the molecule may involve unexcited products of dissociation; such a case probably occurs in the absorption spectra of the oxides of the second group[20]. Further, if the number of valencies and atoms is increased, it becomes more and more probable that a repulsive curve originates in the level of the unexcited separated atoms besides the attractive curve of the ground state (this case may be considered as the same, i.e. as an intersection at large internuclear distances). Considering the figures of table 2, we expect the difference $D_0 - D_B$ to increase from Cl to Br to I, since the respective energies of excitation ($^2P_{\frac{1}{2}}$–$^2P_{\frac{3}{2}}$) are 2, 8·7 and 21·6 kcal./mol. This is indeed indicated in the series PCl_3, PBr_3, and PI_3. The heavier molecules, however, do not follow this rule; and the absolute figures, say of SbI_3, do not permit one to deduct 21·6 kcal./mol. from the value of D_0; unless it becomes possible to reduce the thermochemical figures as a result of new measurements, it seems probable that this steep repulsive curve originates in the level of the unexcited dissociation products. This is also indicated by PBr_3, where the second region of absorption seems to represent the dissociation into PBr_2 and excited Br. Furthermore the steepness of the repulsive curve, which is evident from the width of the absorption region, also indicates that it will run down to the level of the unexcited atoms. SbOCl behaves like other molecules of this series, and the mean bond energies

indicate that it is the Cl atom which is removed first, the mean energy of the $Sb^{III}=O$ bond being too large.

As to the molecules formed by the pentavalent atoms of the fifth group, it can be seen that the D_0 values agree better with the D_T than with the D_B values. This is not so apparent for cases where the D_T values refer to the dissociation of two halogen atoms, but the agreement is very good indeed where a single O atom is split off, as in SO_2Cl_2, SO_3, and TeO_3. In all these cases the first region of selective absorption represents the transition from the ground state to a flat repulsive curve, which originates in the ground level of that molecule in which the valency state of the central atom is diminished by 2. The products of dissociation are unexcited atoms and molecules. The less satisfactory agreement in cases where two halogen atoms are removed simultaneously finds its explanation, if we consider that the energy diagram of such a process can hardly be approximated any longer by a two-dimensional Franck-Condon diagram. Not much is known at present about such conditions, but it seems probable that the repulsive plane in question may be deformed by the presence of the second halogen atom. For N_2O_5 the case is slightly different. We are able to calculate thermochemically the energy of the dissociation process $N_2O_5 \rightarrow N_2O_4+O$ or $N_2O_5 \rightarrow 2NO_2+O$. But N_2O_4 is formed by polymerization of two NO_2 molecules, $O_2N—NO_2$, whereas N_2O_5, the normal derivative of pentavalent nitrogen, has the formula $O_2N—O—NO_2$. Since it is improbable that the middle O atom will be split off, the remaining N_2O_4 radical will possess the formula $O_2N—O—NO$, as distinct from the N_2O_4 molecule. In this case therefore D_B approaches nearer to D_0 than to D_T, which in reality belongs to a different molecule.

As to the molecules of the di- and tetravalent atoms of the sixth group the agreement of the energy value of the long-wave limit with thermochemical and band-spectroscopic data has already been commented upon. The photodissociation of these molecules clearly indicates that the bond energies remain almost unchanged in the transition from diatomic to polyatomic molecules[14]. This seems to be connected with the fact that the elements of the sixth group form diatomic molecules, which, according to the pair-bond interpretation of the method of molecular orbitals, already possess two free valencies.

§ 5. CONCLUSIONS

Even a preliminary theoretical interpretation of the behaviour of such higher polyatomic molecules in the process of photolytic dissociation has to pay regard to the following points: (1) Molecules formed by atoms of the fifth and sixth group in their maximal state of valency dissociate in such a way that the dissociation products are unexcited atoms and an unexcited saturated molecule formed by the central atom in its next lower state of valency. (2) The thermochemical energies of these dissociation processes are considerably smaller than the corresponding mean bond energies. (3) The magnetic properties of these molecules show that at least one of the products of *adiabatic* dissociation is excited. (4) Molecules formed by

trivalent P, etc., and by di- and tetravalent S dissociate into atoms and radicals which are probably also unexcited. The repulsive curve is steep in the case of derivatives of trivalent P and similar molecules and rather flat for molecules formed by di- and tetravalent S. (5) The mean bond energies are always smaller than the energy value of the long-wave limit.

Considerations (1), (2), and (3) together indicate clearly that the flat repulsive curve which produces the photodissociation of these molecules of higher valency is intersected by the curve of the adiabatic dissociation. The same curve of adiabatic dissociation of the molecules of lower valency state in their ground state, however, involves unexcited radicals and atoms. This is schematically shown in figures 6 and 7, which represent the energy levels of PBr_3 and SO_3 and their constituent atoms. The diagram (figure 6) for PBr_3 is simple and exactly as expected; from the level of the separated system $PBr_2 + Br$ two curves originate, one attractive which

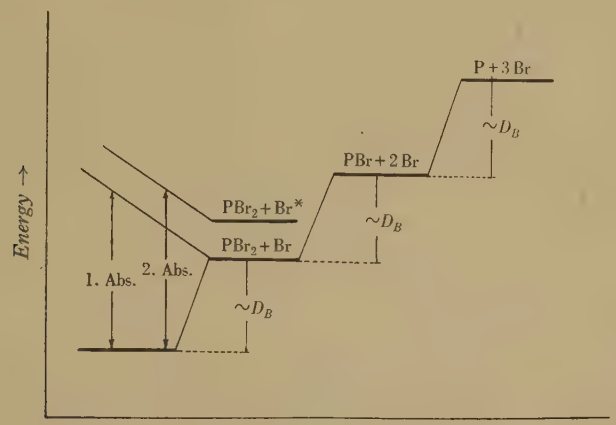

Figure 6.

ultimately forms the ground level of PBr_3, and one repulsive which is the final state for the first region of selective absorption; the second region suggests a second repulsive curve, involving an excited Br atom. This is not so in figure 7, where the ground level of SO_3 does not form part of the same system of ground states as that of SO_2. The second region of absorption is correlated to the process $SO_3 \rightarrow SO_2 + O(^1D)$, and this indicates that the ground state of SO_3 involves an excited SO_2 molecule. The true bond energy of SO_3 cannot therefore be compared either to D_T or to $D_B(SO_3) = \frac{1}{3}D(SO_3)$, since the adiabatic dissociation certainly does not lead to four unexcited atoms. This view, which alone appears to be able to cover all the four points mentioned above, was stated earlier for the explanation of such phenomena[3]. It was then suggested that the fact, which is now rather certain, that no attractive curve originates in the level of unexcited $SO_2 + O(^3P)$ or $O(^1D)$, may be connected with the repulsive character of the s^2 group, the "lone pair" of S, which has to become active during the formation of SO_3. This, of course, cannot be proved by the present experiments. We can only say that at least one of the four separated

atoms S+3O involved in the adiabatic formation or dissociation of SO_3, will be excited, but we do not know which atom it is and in which way the excitation takes place. But this hypothesis seems to be quite probable, since the repulsive character of the s^2 group is theoretically clear beyond doubt, and has been experimentally confirmed by the band spectra of molecules formed by atoms of the second group, and also by the extremely high energy of adiabatic dissociation of CO_2[22]. Apparently CO_2 is not a single case, but according to the continuous absorption spectra we may expect all molecules to behave similarly, if formed by atoms of the higher groups in their maximal state of valency.

The difference in steepness of the repulsive curves for the different types of molecules remains to be explained; the slope obviously depends on various factors and a full interpretation is not yet possible. But we may say that in a case like PCl_3, where both the ground state and the repulsive curve originate in the same level,

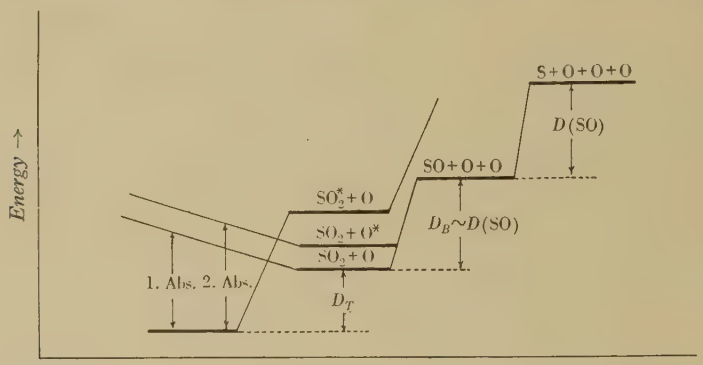

Figure 7.

probably of an unexcited atom and an unexcited radical, a steep repulsive curve may be expected. This case is similar to that of the formation of H_2; here Heitler and London's calculation[23] has shown, that on account of the removal of the degeneracy the original energy value of the degenerated system H+H is replaced by two new energy levels, one lower and one higher than the original common one. On decreasing internuclear distance these two levels form the ground state and a repulsive state respectively, and the slope of the potential curve of the latter will be very steep indeed on account of wave-mechanical repulsion. The absorption spectra of molecules like CH_3Cl are also of interest in this connexion[4], since they show the same type of steep repulsive curves, and conditions are somewhat clearer in such a case, because the CH_3 radical will better approximate a "united atom". We may term these two the "bonding" and the "anti-bonding" curves more or less in accordance with the Herzberg-Mulliken terminology. From the level of the system SO_2+O, however, only one curve originates, which is not split into two and may be considered neither as bonding nor as anti-bonding but as non-bonding. Here the Van der Waals forces predominate, rendering the curve flat. But such a view does not yet explain the small slope of the curve in molecules like $SOCl_2$ nor the steepness

f it in molecules like PCl_5. As pointed out above, we believe at present that the former case is connected with the existence of free valencies in the molecule SO, the latter with the greater complexity of a multi-dimensional Franck-Condon model.

REFERENCES

(1) Butkow, K. *Z. Phys.* **90**, 810 (1934).
(2) Trivedi, H. *Bull. Acad. Sci. Allahabad*, **3**, 23, 229 (1934).
(3) Samuel, R. *Report on Absorption Spectra and Chemical Linkage*, Ind. Acad. Sci. (Bangalore), Symposium (1934). Cf. also *Curr. Sci.* **3**, 549 (1935).
(4) Herzberg, G. and Scheibe, G. *Z. phys. Chem.* B, **7**, 390 (1930) and the discussion in Iredale, T. and Mills, W., *Proc. roy. Soc.* A, **133**, 430 (1931).
Henrici, A. *Z. Phys.* **77**, 35 (1932).
Hukumoto, M. *Phys. Rev.* **42**, 313 (1932).
Iredale, T. *Z. Phys. Chem.* B, **20**, 340 (1933).
Rehman, R. A., Samuel, R. and Sharf-ud-Din. *Indian J. Phys.* **8**, 537 (1934).
Bayliss, N. S. *Nature*, Lond., **136**, 264 (1935).
(5) Walden, P. *Z. Elektrochem.* **14**, 173 (1908).
(6) Forcrand, R. de. *C.R. Acad. Sci.*, Paris, **133**, 368, 513 (1901).
(7) Franck, J. *Trans. Faraday Soc.* **21**, 526 (1925).
Kuhn, H. *Z. Phys.* **39**, 77 (1927) (slight later corrections).
(8) Herzberg, G. and Sponer, H. *Z. Phys. Chem.* B, **26**, 1 (1934).
Buettenbender, G. and Herzberg, G. *Ann. Phys.* **31**, 577 (1935).
(9) Herzberg, G. *Ann. Phys.* **15**, 677 (1932).
(10) Lessheim, H. and Samuel, R. *Proc. Ind. Acad. Sci.*, Bangalore, **1**, 623 (1935) (Sect. x and xi).
(11) Frerichs, R. *Phys. Rev.* **36**, 398 (1930).
Herzberg, G. *Z. Phys. Chem.* B, **10**, 189 (1930); *Naturwissenschaften*, **20**, 577 (1932).
(12) Rosen, B. *Z. Phys.* **43**, 69 (1927).
(13) Rao, K. R. and Krishnamurti, S. G. *Proc. roy. Soc.* A, **145**, 694 (1934).
Ruedy, J. E. and Gibbs, R. C. *Phys. Rev.* **46**, 880 (1934).
Bartalt, O. *Z. Phys.* **88** (1934).
(14) Asundi, R. K. and Samuel, R. *Proc. phys. Soc.* **48**, 28 (1935).
(15) Urey, H. C., Dawsey, L. H. and Rice, F. O. *J. Amer. chem. Soc.* **51**, 3190 (1929).
(16) Dutta, A. K. and Sen Gupta, P. K. *Proc. roy. Soc.* A, **139**, 397 (1933).
(17) Goodeve, C. F. and Wallace, Janet I. *Trans. Faraday Soc.* **26**, 254 (1930).
Finkelnburg, W., Schumacher, H. J. and Stieger, G. *Z. Phys. Chem.* B, **15**, 127 (1932).
(18) Dutta, A. K. *Proc. roy. Soc.* A, **137**, 366 (1932).
(19) Hunter, R. F. and Samuel, R. *Rec. Trav. chim. Pays-Bas*, **54**, 114 (1935).
(20) Lessheim, H. and Samuel, R. *Z. Phys.* **84**, 637 (1933); **88**, 276 (1934); *Phil. Mag.* **21**, 41 (1935).
(21) Herzberg, G. *Z. Phys.* **57**, 601 (1930).
Franck, J. *Naturwissenschaften*, **19**, 217 (1931).
Franck, J. and Kuhn, H. *Bull. Acad. Sci. Allahabad*, **2**, 223 (1932). Cf. R. Samuel, ref. (3).
(22) Lessheim, H. and Samuel, R. *Ind. Acad. Sci.*, Bangalore, **1**, 623 (1935); *Proc. phys. Soc.* **46**, 523 (1934) and literature mentioned there.
(23) Heitler, W. and London, F. *Z. Phys.* **44**, 455 (1927).

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SOME EXPERIMENTS WITH NEUTRONS HAVING THERMAL ENERGIES

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ABSTRACT. Moon and Tillman have found a large influence of temperature upon the properties of neutrons within a cavity in a block of paraffin wax; on the other hand, Dunning, Pegram, Fink and Mitchell, using a lithium-lined ionization chamber, found no detectable influence of temperature upon the number of disintegrations of lithium produced by neutrons leaving the surface of a can of water which contained a radon-beryllium source of fast neutrons.

This apparent discrepancy has been investigated; the various explanations hitherto proposed have been found inadequate, and the difficulty has been resolved by an experimental proof that the activity produced in a specimen of silver when it is exposed within a thin-walled wax cylinder to the neutrons emerging from a large block of wax shows nearly as great a dependence upon the temperature of the cylinder as when the system is exposed within a cavity in the large block. The failure to find effects of temperature with the emergent neutrons was therefore due not to an absence of neutrons having thermal velocities but to an ineffective means of changing the temperature of these neutrons.

§ 1. INTRODUCTION

The neutrons produced in the nuclear reaction ${}^{9}_{4}\mathrm{Be}+{}^{4}_{2}\mathrm{He}={}^{12}_{6}\mathrm{C}+{}^{1}_{0}n$, when allowed to diffuse through paraffin wax, may have their velocities reduced to such an extent by collisions with the hydrogen nuclei present that they are able to attain some measure of thermal equilibrium with the wax. This fact was established in the following way[1]. A radon-beryllium source of neutrons was placed in a large block of wax some 10 cm. from a cavity whose walls, to a depth of about 1 cm., could be kept either at room-temperature or at the boiling-point of liquid oxygen. A Geiger counter was used to measure the β-ray activity induced in a thin specimen of silver which had been exposed for a known time in the cavity. When the temperature of the walls was 90° K. the activity obtained was considerably greater than when they were at room-temperature. Two conclusions are to be drawn from this experiment. Firstly, many of the neutrons crossing the cavity and responsible for the activity induced in the specimen must have energies of the order of those of thermal agitation (0·03 volt). Secondly, the cross-section of the silver nucleus for capture of a neutron must increase with decreasing velocity of collision. Measurements showed that the nuclei of rhodium, copper, iodine, dysprosium, and other elements behave, qualitatively at least, in a manner similar to that of the silver nucleus. It was typical of these experiments that the specimens were always

irradiated inside cavities in the paraffin wax. If the thickness of the cooled wax was greater than 1 cm. the effect of its change of temperature was less, owing to increased absorption by the cold wax: with very thick layers (4 cm. or more) the effect of temperature was zero or even reversed.

Dunning, Pegram, Fink and Mitchell[2], who were also searching for evidence of the existence of thermal neutrons, used a different geometrical arrangement. The source of fast neutrons was placed inside a large can of water, but the detector of the slow neutrons, a lithium chamber, was at some distance away outside. The whole of the water could be cooled from 373° to 90° K. The number of disintegrations of lithium nuclei per minute showed no definite increase with the cooling of the water. The absorption by a thin sheet of cadmium of the neutrons emerging from the water was measured also: a very small increase in the absorption coefficient of this element was noted when the temperature of the water was lowered. In order to meet the objection involved in the use of thick layers of cooled material, these authors[3] later made further measurements with lithium detection and cadmium absorption, cooling thin layers instead of thick. No significant differences were observed.

Four explanations of their results are possible. (1*a*) Lithium may not detect neutrons having thermal velocities; (1*b*) the detection of neutrons by lithium and their absorption by cadmium, though extending to thermal velocities, may be insensitive to change of velocities; (2*a*) not many of the neutrons coming from the water may have thermal velocities; (2*b*) thermal neutrons, though present, may not change their temperature appreciably in passing through a thin slab of cold wax. Of these possible explanations (1*a*), (1*b*) and (2*a*) have been pointed out by Dunning.

The experiments to be described in this paper may be summarized as follows. (i) Dunning's experiment was repeated with detectors of silver and of boron, for which explanations (1*a*) and (1*b*) were already known to be untenable. (ii) Explanations (1*a*) and (1*b*) were tested for the cases of lithium and cadmium by measurements of the absorption by these elements of neutrons whose velocities were known to be thermal. (iii) Explanations (1*a*) and (1*b*) having now been dismissed, calculations were made[7] which showed (2*a*) to be improbable. Explanation (2*b*) was therefore investigated and was found to agree with experiment.

The experiments will now be described in detail.

§ 2. MEASUREMENTS MADE OUTSIDE A BLOCK OF WAX

For the first experiments a thin specimen of silver was used as a detector of slow neutrons. The apparatus is shown in figure 1. A radon-beryllium source of neutrons was placed at the centre *C* of a fairly large block of wax *W*, and one or other of two thin slabs of wax, identical in all respects but temperature, was interposed between *W* and *S* at *D*. One slab was kept at room-temperature, 290° K., and the other at the boiling-point of liquid oxygen, 90° K.

The specimen of silver was placed at *S* and exposed to the beam of slow neutrons

for 1 min. with the slab at D at room-temperature. A measure of the β-ray activity induced in the specimen was obtained in the usual way with a Geiger counter, amplifier, and mechanical counter. When the cold slab was substituted the activity was greater in the ratio 1·06 : 1. The probable error was $\pm 0{\cdot}04$, so that the increase is scarcely definite.

A boron-lined ionization chamber was next placed at B and used as a detector of slow neutrons. It was connected to a linear amplifier and mechanical counter. Runs having a duration of 1 min. were made, the warm and cold slabs being placed

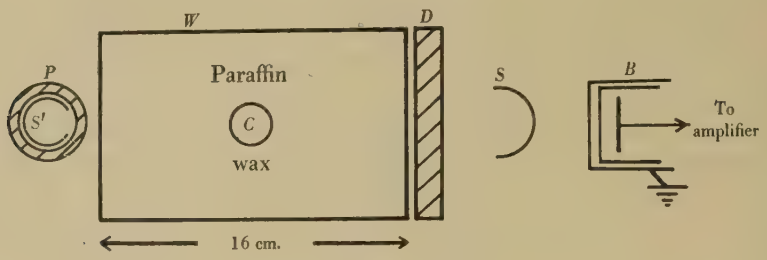

Figure 1.

at D in turn. Although the number of α particles recorded in all was well over 10,000, the rate of counting with the cold slab at D was no greater than with the warm slab. The final ratio was

$$\frac{\text{count with cold slab}}{\text{count with warm slab}} = 1{\cdot}01 \pm 0{\cdot}03.$$

Thus a change in the temperature of the outer layers of the paraffin wax has little influence upon the numbers of neutrons recorded by silver and boron detectors. Since[1] silver and boron respond to thermal neutrons and are sensitive to changes in their velocity, explanations (1 *a*) and (1 *b*) cannot hold for these elements, though they still might hold for the lithium detector used by Dunning.

§ 3. ABSORPTION MEASUREMENTS

In order to see whether explanations (1 *a*) or (1 *b*) may yet hold for lithium and cadmium, an apparatus similar to that used by Moon and Tillman in their original experiments on temperature effects was set up, figure 2. The hollow cylinder of wax P inside the Dewar vessel D had a wall-thickness of 1 cm. The source of neutrons C was about 8 cm. from D. A thin specimen of silver was irradiated at S with the cylinder at room-temperature and the β-ray activity was measured. A lithium absorber in the form of a cylinder was then placed at A, around S. The activity induced in the silver was again measured, after irradiation at S with A in position. These two measurements were repeated with P at 90° K. The transmission factors were calculated in each case.

Boron and cadmium absorbers also were investigated. The results are given in table 1. Use was made of the two periods of silver, 22 sec. and 2·5 min. For the

measurements with the shorter period the lithium absorber contained 0·3 g./cm.², while for the longer period it contained 0·2 g./cm.² The boron absorber contained 0·03 g./cm.² and the cadmium 0·015 g./cm.² If, for the sake of comparing the behaviour of the three elements, we assume the absorption in all cases to follow an exponential law we can obtain λt for any of the elements used, where λ is the absorption coefficient (cm.²/g.) and t is the mass of the absorber (g./cm.²). If λ_1 refers to room-temperature neutrons and λ_2 to 90°-K. neutrons, λ_2/λ_1 is calculable. This ratio has been included in the table.

λ, t
λ_1
λ_2

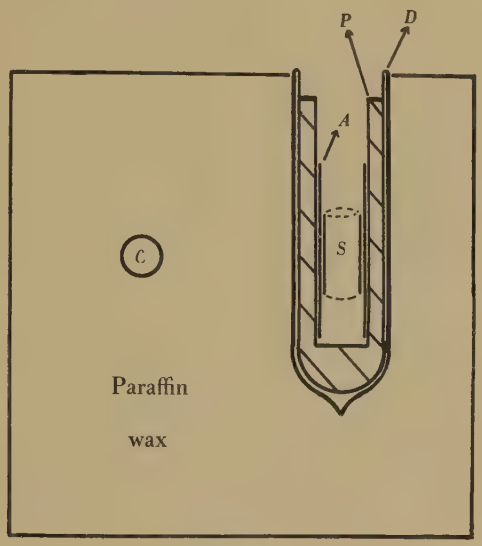

Figure 2.

Table 1

Absorber \ Detector		Silver, 22 sec. period	Silver, 2·5 min. period
Lithium	290° K.	$0{\cdot}38_8 \pm 0{\cdot}01_6$	$0{\cdot}51_0 \pm 0{\cdot}01_7$
	90° K.	$0{\cdot}30_3 \pm 0{\cdot}01_5$	$0{\cdot}41_0 \pm 0{\cdot}01_3$
	λ_2/λ_1	1·27 ± 0·07	1·32 ± 0·06
Boron	290° K.	$0{\cdot}44_5 \pm 0{\cdot}02$	$0{\cdot}39_8 \pm 0{\cdot}02$
	90° K.	$0{\cdot}37_4 \pm 0{\cdot}02$	$0{\cdot}32_8 \pm 0{\cdot}01_5$
	λ_2/λ_1	1·21 ± 0·08	1·21 ± 0·07
Cadmium	290° K.	—	$0{\cdot}50_5 \pm 0{\cdot}01_5$
	90° K.	—	$0{\cdot}43_0 \pm 0{\cdot}01_5$
	λ_2/λ_1	—	1·24 ± 0·06

The ratio of the activity induced in the specimen with P at 90° K. to that induced with P at 290° K., with no absorber present, was $1{\cdot}27 \pm 0{\cdot}04$ for the shorter period of silver and $1{\cdot}35 \pm 0{\cdot}04$ for the longer. These figures are in agreement with the previous results[1].

The table tells us at once that the absorption of slow neutrons by lithium and cadmium is appreciable for very low velocities of the neutron, and is sensitive to changes of these velocities. Explanations (1*a*) and (1*b*) cannot be true, therefore, for any of the elements silver, boron, lithium and cadmium.

Now explanation (2*a*) is improbable for two reasons. The experiments of Dunning[4] and others with a velocity-selector show directly the presence of some neutrons having thermal energies amongst those emerging from a face of a block of wax. Moreover, Moon's calculations[7] indicate that quite a fair proportion of the activity induced in a silver specimen exposed outside a block of wax should be due to thermal neutrons.

§ 4. THE PROPOSED EXPLANATION

We are left with the last possibility, (2*b*). It was realized that the inside and outside experiments differed in that in the former case the specimen was completely surrounded by the wax layer. At the suggestion of Dr P. B. Moon I tried the following experiment. A source of fast neutrons was placed at the centre of a large block of wax *W* and a hollow cylinder of wax *P* of wall-thickness 0·6 cm. just outside, figure 1. The specimen was irradiated at *S'*. The activity induced in a silver specimen was increased by a factor of $1{\cdot}28 \pm 0{\cdot}07$ when the cylinder *P* was cooled from 290 to 90° K. A separate experiment showed that very little of the activity induced was due to fast neutrons scattered in *P*.

We conclude that many of the neutrons reaching *P* from *W* have energies as low as those of thermal agitation. It is from the results obtained with a cylinder of wax and not from those with a block of wax that we are able to draw this conclusion. A thermal neutron leaving *W* and entering *P* may cross and recross the hollow of the cylinder many times before being captured by the specimen at *S'*. Its chance of reaching thermal equilibrium with *P* is high. Had *P* been used inside a cavity, such as that occupied by the Dewar vessel in figure 2, measurements with a silver detector having a period of 22 sec. would have given an increase of activity of about 1·33. Whether the value of $1{\cdot}28 \pm 0{\cdot}07$ is definitely less than that to be obtained with *P* inside is a question of some importance, but a more accurate determination of this value (e.g. to within $\pm 0{\cdot}02$) would involve the counting of a very large number of particles.

§ 5. DISCUSSION OF RESULTS

The neutrons that are highly absorbed by silver, called Group A by Fermi[5], are more prominent outside a block of wax than inside: they are believed to have energies above those of thermal agitation. Again, when silver is exposed inside a cavity in a block of wax, the induced activity can be reduced to about one-eighth its original value by surrounding the specimen with a thick (0·5 mm.) sheet of cadmium: if, on the other hand, the silver be exposed outside a block of wax, the sheet of cadmium when interposed between wax and silver reduces the activity only to 45 per cent of its original value. These two experimental results suggest that

thermal neutrons are present in rather smaller proportions outside than inside a block of wax. Moon's calculations support this suggestion.

Lithium, cadmium, and boron have all shown increased absorption of slow neutrons with decreasing velocity of the neutron. Boron has already been mentioned[1]. Westcott and Niewodniczański[6], making measurements similar to those described here, have reported a value of $1{\cdot}07 \pm 0{\cdot}04$ for λ_2/λ_1 in cadmium. They stated that their absorber was rather thick, 0·039 g./cm.^{2}; the discrepancy between their value and that obtained here, $1{\cdot}24 \pm 0{\cdot}06$, is mainly due to the assumption of an exponential absorption. The thicker the absorber, the less accurate is this assumption.

Much of the recent work on the properties of slow neutrons has been done with the beam of neutrons emerging from a block of wax. It was important that we should have some knowledge of the energy-distribution in such a beam. Some of the experiments had pointed to the presence of thermal neutrons in the beam, but Dunning's temperature experiment had remained outstanding. It was the main purpose of the present work to inquire into the apparent discrepancy between that temperature experiment and those of Moon and Tillman. That discrepancy has now been removed.

§ 6. ACKNOWLEDGMENTS

The radon was kindly given by the Radiology Committee of the Medical Research Council: I am grateful to Prof. S. Russ for arranging the supplies. I should like also to thank Dr C. E. Wynn-Williams for the loan of the linear amplifier and mechanical counter mentioned in § 2.

REFERENCES

(1) Moon and Tillman. *Proc. roy. Soc.* A, **153**, 476 (1936).
(2) Dunning, Pegram, Fink and Mitchell. *Phys. Rev.* **48**, 265 (1935).
(3) Dunning, Pegram, Fink and Mitchell. *Phys. Rev.* **49**, 103 (1936).
(4) Dunning, Pegram, Fink, Mitchell and Segrè. *Phys. Rev.* **48**, 704 (1935).
(5) Fermi and Amaldi. *Ric. Scient.* 14 December 1935.
(6) Westcott and Niewodniczański. *Proc. Camb. phil. Soc.* **31**, 617 (1935).
(7) Moon. Page 648 of this volume.

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ON THE PASSAGE OF NEUTRONS THROUGH PARAFFIN WAX

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ABSTRACT. The velocity-distribution of neutrons passing through paraffin wax is investigated on the assumption that the collisions made before thermal velocity has been reached are elastic collisions with protons. Within the body of the wax, and provided the variation of free path with velocity is not rapid in the neighbourhood of thermal velocities, thermal neutrons outnumber all others in the ratio of about P to 1, where P is the average number of collisions made by a thermal neutron before it is absorbed. According to Bjerge and Westcott, P is of the order of 80. The number of neutrons crossing unit area is estimated; in this case also the majority have thermal velocities. The velocity-distribution of neutrons emerging from the surface differs from that in the interior, thermal neutrons, though probably still in the majority, being less prominent under the former conditions. The ratio of the flux of thermal neutrons in the interior to that at the surface is calculated and shows satisfactory agreement with the experimental value of about 13 to 1 obtained when the neutrons are estimated from the artificial radioactivity of silver.

§ 1. INTRODUCTION

The purpose of this communication is to gather together some calculations regarding the equilibrium of neutrons with a hydrogen-containing medium. Since water and paraffin wax are widely used for reducing the velocities of fast neutrons, attention will be concentrated upon these two substances, which in this connexion have properties so similar[1] that they will be treated as identical. The experimental facts upon which numerical calculations will have to be based, and those which the calculations will be used to interpret, are not yet known with any great accuracy; there is consequently neither the possibility nor the need for anything more than an estimate of the orders of magnitude concerned. The main object of the calculations is to obtain some idea of the numbers of neutrons of different velocities which are to be expected in the flux of neutrons passing through, or emerging from, a large block of wax irradiated uniformly by very fast neutrons such as those which may be obtained by bombarding beryllium with α particles.

When a uniform supply of fast neutrons is introduced into an infinite bulk of matter, there is set up an equilibrium distribution of velocities, determined by the condition that the number of neutrons entering any velocity group as a result of scattering shall be equal to the number leaving that group as a result either of scattering or of absorption. The scattering of neutrons in wax is due mainly to the hydrogen nuclei; absorption, whether due to hydrogen or to carbon, is believed to

be so small that a neutron having initially a kinetic energy of a million electron-volts or more has a high probability of reaching thermal velocity before being captured. About eighteen collisions with particles of the same mass will on the average reduce the energy of a two-million-volt neutron to the 0·03 volt characteristic of thermal agitation at ordinary temperature; Bjerge and Westcott[1] estimate from their experiments that about eighty collisions are made by the average slow neutron before it is captured.

We may therefore hope to make an approximate calculation of the equilibrium velocity-distribution within a large bulk of wax on the following assumptions: (i) That the collisions made before thermal velocity has been reached are elastic collisions with protons which may be regarded as stationary. The colliding particles will be treated as elastic spheres of equal mass.* (ii) That eighty further collisions, on the average, are made after thermal velocity has been reached.

The velocity-distribution of the thermal neutrons will be very nearly Maxwellian, so in order to describe them completely we need specify only their total number. A more or less arbitrary upper limit C must be set to the velocities which are to be regarded as thermal; this will be taken at twice the average thermal velocity $\bar{c}$. At room-temperature, C will correspond to an energy of about 0·13 V.; a two-million-volt neutron will have to make about sixteen collisions with stationary protons in order to reach such an energy. In default of a suitable positive expression to include neutrons of all energies from 0·13 V. upwards, such neutrons will be called "non-thermal". This arbitrary division will lead to some error in the estimate of the velocity-distribution in the neighbourhood of the velocity C. Velocities of that order seem likely to be of considerable interest[2] and would deserve special investigation, but since the present discussion is concerned only with the broad outline of the velocity-distribution it would be unprofitable to deal with the matter here.

C

$\bar{c}$

§ 2. VELOCITY-DISTRIBUTION FOR NON-THERMAL NEUTRONS IN THE INTERIOR OF A LARGE BLOCK OF WAX

Let S neutrons of velocity U be introduced every second into every unit volume of an infinite bulk of wax; let the mean free path for a neutron of velocity u be $\lambda(u)$, and until a neutron has reached the velocity C (where $C \ll U$) let the laws of collision be as for the elastic impact of a moving sphere upon a stationary sphere of equal mass. The chance that in such a collision a neutron whose velocity was previously v shall acquire a velocity lying between u and $u+du$ is easily shown to be $(2u/v^2)\,du$. If $N(v)\,dv$ be the number of neutrons per unit volume having velocities between v and $v+dv$, the number of collisions made by neutrons of this class is

S, U

u, λ

v

N

$$\frac{v}{\lambda(v)} . N(v)\,dv$$

* The neutron is heavier than the proton by about one part in a thousand. This will make very little difference to the present calculations, but it will mean that a neutron cannot reach thermal velocity in a single elastic collision, because even if the collision is precisely head-on the neutron will retain a four-thousandth part of its original energy.

per cm.^{3} per second, and the number of neutrons thereby transferred to class u is

$$\frac{v}{\lambda(v)}.N(v)\,dv\frac{2u}{v^2}\,du.$$

The total rate of gain of class u is therefore

$$\int_{v=u}^{v=U}\frac{N(v)}{\lambda(v)}.\frac{2u}{v}\,du\,dv$$

per cm.^{3} per sec. Since absorption of the neutrons is being neglected, the rate of loss of class u is equal to the number of elastic collisions made in a second by neutrons of this class, viz.,

$$\frac{u}{\lambda(u)}.N(u)\,du.$$

The velocity-distribution of the neutrons, within the limits $U>u>C$, must therefore satisfy the equation

$$\int_{v=u}^{v=U}\frac{N(v)}{\lambda(v)}.\frac{2u}{v}\,du\,dv=\frac{u}{\lambda(u)}N(u)\,du.$$

This equation is to be solved subject to the condition that the number of neutrons passing through any velocity group in unit time shall be equal to the number S which are introduced at the upper end of the velocity spectrum. It may be verified that when $u\ll U$ (that is, after the first few collisions) the requirements are satisfied by the velocity-distribution

$$N(u)\,du=\frac{2S\lambda(u)}{u^2}\,du^* \qquad \ldots\ldots(1).$$

Since u^2 appears in the denominator, there is a preponderance of the slower non-thermal neutrons whose velocities are not very much above the minimum velocity C to which these calculations apply. If, in and just above the thermal range of velocities, λ does not vary rapidly with u, the total number Q_N of non-thermal neutrons will not be far from that given by

Q_N

$$Q_N=\int_C^U\frac{2S\lambda_0}{u^2}\,du=\frac{2S\lambda_0}{C},\ \text{since } U\gg C \qquad \ldots\ldots(2),$$

where λ_0 is the free path for neutrons of thermal velocity.

λ_0

The number of neutrons of class u crossing a square centimetre (from both sides) in a second is

$$\frac{u}{2}.N(u)\,du=\frac{S\lambda(u)}{u}\,du.$$

The preponderance of the lower velocities is here less marked, and it is less justifiable to take λ as constant and equal to λ_0; however, since λ is of the order of a few millimetres at thermal velocities and rises only to a few centimetres for fast

* Amaldi and others[3] have given the equation

$$N(u)\,du=\text{const.}\times\frac{u\,du}{(u+\lambda/T)^3}$$

for the case where λ is constant but absorption occurs, the absorption law being such that a neutron has a mean life T which is independent of u.

neutrons whose velocities are 10^4 times as great, the assumption of a constant free path of the thermal value is not likely to lead to an entirely wrong order of magnitude. The flux M_N of non-thermal neutrons across unit area is then given by the equation M_N

$$M_N = \int_C^U \frac{S\lambda_0}{u}.du = S\lambda_0 \log_e \frac{U}{C} \qquad \text{.....(3).}$$

In order to form some estimate of the effect of a variable free path, one need only realize that if the free path for any range of velocities be increased n times each neutron stays n times as long within those limits of velocity, and the number of such neutrons is simply increased n times, other velocities being quite unaffected. As an approximation to the (unknown) law of variation of free path with velocity, let us make the rather extreme assumption that λ is equal to five times λ_0 at all velocities above C, the drop to the thermal value at this velocity being sudden. Then instead of equation (2) we shall simply have

$$Q'_N = \frac{10S\lambda_0}{C} \qquad \text{.....(4).} \qquad Q'_N$$

The flux of neutrons will also be increased five times, so equation (3) must be replaced by

$$M'_N = 5S\lambda_0 \log_e \frac{U}{C} \qquad \text{.....(5).} \qquad M'_N$$

§ 3. NUMBERS OF THERMAL NEUTRONS

Since there is supposed to be no absorption at velocities above thermal velocity, the number of neutrons which reach that velocity is equal to the number S which are introduced as fast neutrons. The number present in unit volume is therefore ST, where T is the mean life of a neutron after thermal velocity has been reached. If T the number of collisions made before absorption be denoted by P, then P

$$T = \frac{\lambda_0 P}{\bar{c}},$$

and the number Q_T of thermal neutrons per unit volume is given by Q_T

$$Q_T = \frac{S\lambda_0 P}{\bar{c}} \qquad \text{.....(6).}$$

The number crossing unit area (from both sides) per second is M_T where M_T

$$M_T = \frac{\bar{c}}{2}.Q_T = \frac{1}{2}S\lambda_0 P \qquad \text{.....(7).}$$

Equations (6) and (7) are independent of the values of the free path at velocities greater than C. If, as was first assumed in § 2, λ is constant and equal to λ_0, then, from equations (2) and (6), the ratio between the numbers of thermal and non-thermal neutrons is

$$\frac{Q_T}{Q_N} = \frac{C}{2\bar{c}}.P = P \qquad \text{.....(8),}$$

while the ratio of the flux of thermal neutrons to the flux of non-thermal neutrons, from equations (3) and (8), is given by

$$\frac{M_T}{M_N}=\frac{P}{2\log(U/C)} \qquad \text{.....(9).}$$

On the second assumption, that the free path for non-thermal neutrons is five times that for thermal neutrons, each of these ratios is divided by five, so we have

Q'_T

$$\frac{Q'_T}{Q'_N}=\frac{P}{5} \qquad \text{.....(10)}$$

M'_T and

$$\frac{M'_T}{M'_N}=\frac{P}{10\log(U/C)} \qquad \text{.....(11).}$$

Since P is about 80, the number of thermal neutrons is on the first assumption 80 times the number of faster neutrons; on the second assumption this ratio decreases to 16. The ratio U/C is about 6×10^3, and its logarithm is about 8, so the assumption of constant free path gives the flux ratio as about 5; the second assumption would lead to the conclusion that the flux of thermal neutrons is about equal to that of non-thermal neutrons. One would expect the actual value to lie somewhere between these limits; that is to say, thermal neutrons, though not so predominant as when the numbers per unit volume are considered, will constitute a definite majority of the total number which cross any plane in the wax.

§ 4. THE NEUTRONS EMERGING FROM THE SURFACE OF A LARGE BLOCK OF WAX

Many experiments upon the properties of slow neutrons have been made by using the neutrons which emerge from the surface of a block of wax in which is embedded a source of fast neutrons; it is therefore important to consider how the numbers and velocities of the emergent neutrons will differ from those of the neutrons crossing a cavity within the block.

If two semi-infinite blocks are placed face to face so as to leave a thin cavity, the neutrons crossing the cavity may be divided into two classes, (i) those which are making their first transit—that is to say, those which would have emerged from either block had the other block been absent, and (ii) those which have previously made one or more transits—that is, those of class (i) which are scattered back into the cavity after once having emerged from the parent block.

Class (i) is composed of twice the number escaping from a free surface; the neutrons of class (ii) must on the whole be slower than those of class (i), since, until thermal velocities have been reached, scattering involves a decrease of velocity. The number of neutrons escaping from unit area of a free surface must therefore be less than half the number crossing unit area from both directions in the centre of the block, and this decrease will be most marked for the lower velocities.

A proper analytical investigation of the loss of neutrons from a free surface would be difficult, even with the simplifications which have already been adopted, but it is possible to gain some useful information without undue labour by following

out the history of typical neutrons generated at different distances from the surface. If the neutron travels a constant distance λ_0 between collisions, the average component of free path measured normal to the surface is $\frac{1}{2}\lambda_0$. Consider now a neutron starting at a distance $\frac{1}{2}h\lambda_0$ from the surface;* the chance that it shall escape after h having traversed p paths in random directions is nearly† the same as the chance p that in a series composed of $+1$ and -1 in random sequence the sum shall first exceed $+h$ at the pth term. The directions of successive paths are however not independent; this persistence of velocity nearly doubles the average rate at which the neutrons diffuse towards the surface,‡ so we may say that the chance that the random series shall first attain a sum in excess of h at its pth term is equal to the chance that a neutron shall escape after p free paths (i.e., after $p-1$ collisions) from a depth of about $h\lambda_0$ instead of $\frac{1}{2}h\lambda_0$. The process of diffusion from a starting-point situated at h free paths below the surface may therefore be roughly imitated by the tossing of a coin; if the balance of heads over tails first exceeds h when p throws have been made, the neutron has escaped with a velocity corresponding to its having made $p-1$ collisions.

Taking as before 16 collisions as sufficient for the attainment of the critical velocity C, equal to $2\bar{c}$, and 80 further collisions as representing the average life of a thermal neutron, we shall say that if p is 16 or less, the neutron has escaped before reaching thermal velocity; if p lies between 17 and 96, the neutron has escaped with thermal velocity, while if p is greater than 96, the neutron has failed to escape before being captured. With the help of Mr J. R. Tillman I traced out 48 series of this nature, and for each of these found at what value of p the neutron would have escaped if it had started at depths $\frac{1}{2}\lambda_0$, $1\frac{1}{2}\lambda_0$, $2\frac{1}{2}\lambda_0$, ... below the surface. Each of these starting-points is the middle of one of an infinite series of layers, each of thickness λ_0, taken parallel to the surface, so this corresponds to an introduction of fast neutrons at a rate of $48/\lambda_0$ per centimetre of thickness.

The total number of escapes was 360, of which 120 took place before the attainment of thermal velocities and the remaining 240 afterwards.§ If the rate of introduction had been S per cubic centimetre per second, the rate of escape of non-thermal neutrons would therefore have been $120.S.\lambda_0/48$ per square centimetre of surface, and that of thermal neutrons would have been $240.S.\lambda_0/48$. Thus for the neutrons emerging from the surface of a large block we have

$$\text{Flux of non-thermal neutrons} = m_N = 2\tfrac{1}{2}\lambda_0 \quad \text{.....(12)}, \qquad m_N$$

and

$$\text{Flux of thermal neutrons} = m_T = 5\lambda_0 \quad \text{.....(13)}. \qquad m_T$$

The ratio m_T/m_N is therefore about 2 : 1 as compared with the ratio M_T/M_N of 5 : 1 found in § 3 for the neutrons within the block. The proportion of thermal neutrons, though less, is thus still quite comparable with the proportion occurring in the flux of neutrons crossing a cavity within the block. The absolute numbers

* h is not supposed to be integral.

† Some error is of course introduced by the assumption that every component free path is equal to the arithmetic mean.

‡ See Jeans, *Dynamical Theory of Gases*.

§ The simple relation between these numbers is fortuitous.

have decreased considerably; P being taken as 80, equations (7) and (13) show that the flux of thermal neutrons is about eight times less outside than inside the block, while the flux of non-thermal neutrons has decreased about three times.

The flux of neutrons through the surface was next investigated on the assumption that the first 16 free paths were five times as long as those made after 16 collisions had taken place. For this purpose it is only necessary to give a five-fold value to each of the first 16 tosses. The number of non-thermal neutrons escaping rose, of course, five times, being now 600, but this depletion of the outer layers naturally entailed a decrease in the number of thermal neutrons escaping; the number actually fell to 103. Remembering that the use of 48 series corresponds to the introduction of fast neutrons at the rate of 48 per (thermal) free path of thickness, m'_N we obtain for the flux m'_N of non-thermal neutrons corresponding to the introduction of S fast neutrons

$$m'_N = 12\lambda_0 S \text{ approximately} \qquad \ldots\ldots(14),$$

m'_T and for the flux m'_T of thermal neutrons

$$m'_T = \text{about } 2\lambda_0 S \qquad \ldots\ldots(15).$$

The decrease in m'_T as compared with m_T is due in great part to the sudden nature of the assumed drop in free path at $u = C$; if the drop is gradual there will be a better chance for the depletion of the surface layers to be made up by the diffusion of the faster thermal neutrons whose free paths would then be of intermediate length; further, there is no reason to suppose that the fall in free path occurs in the immediate neighbourhood of $u = C$, and if it occurs at high velocities the proportion of thermal neutrons emerging will approach more nearly to that obtained on the assumption of constant free path. It is to be concluded, then, that at least a very considerable proportion of the flux of emergent neutrons consists of neutrons of thermal velocities. Whether in any experiment made upon these neutrons the results refer mainly to the thermal or the non-thermal portion of the beam, is a question to which no general answer can be given; it depends upon the sensitivity of the apparatus to neutrons of different velocities.

In table 1 are collected the more important equations which have been derived above, while table 2 gives numerical values of certain important ratios, it being supposed that 80 collisions are made by a thermal neutron before its capture.

§ 5. THE EFFECT OF ABSORPTION OF NON-THERMAL NEUTRONS

The above calculations have been made on the assumption that no neutron is absorbed until it has reached thermal velocity. If a known amount of absorption of faster neutrons does in fact occur, allowance may readily be made for it. For example, a sharp absorption band which removes 10 per cent of the neutrons which have an energy of 100 V. will in every case simply cause a 10-per-cent reduction in the number of neutrons of all lower velocities. The values of m_T/M_T and m'_T/N'_T given above for the inside : outside ratio for thermal neutrons are therefore independent of absorption at velocities above thermal; they depend only upon the

umbers of collisions made before and after thermal velocities have been reached nd upon the law connecting free path with velocity.

able 1. Number and flux of neutrons inside and outside a large block of wax. The rate of introduction of fast neutrons is 1 per cm.^{3} per sec. The values outside the block are for the case of 16 collisions before and 80 after reaching thermal velocities.

	Inside		Outside	
	Free path constant $= \lambda_0$	Free path for non-thermal neutrons $= 5\lambda_0$	Free path constant $= \lambda_0$	Free path for non-thermal neutrons $= 5\lambda_0$
Number of thermal neutrons per unit volume	$Q_T = \frac{\lambda_0 P}{\bar{c}}$	$Q'_T = \frac{\lambda_0 P}{\bar{c}}$	—	—
Number of non-thermal neutrons per unit volume	$Q_N = \frac{2\lambda_0}{C} = \lambda_0/\bar{c}$	$Q'_N = \frac{10\lambda_0}{C} = \frac{5\lambda_0}{\bar{c}}$	—	—
Flux of thermal neutrons through unit area	$M_T = \frac{1}{2}\lambda_0 P$	$M'_T = \frac{1}{2}\lambda_0 P$	$m_T = 5\lambda_0$	$m'_T = 2\lambda_0$
Flux of non-thermal neutrons through unit area	$M_N = \lambda_0 \log_e \frac{U}{C}$	$M'_N = 5\lambda_0 \log_e \frac{U}{C}$	$m_N = 2\frac{1}{2}\lambda_0$	$m'_N = 12\frac{1}{2}\lambda_0$

Table 2. Number and flux ratios; 16 collisions made before and 80 after reaching thermal velocity.

	Free path constant $= \lambda_0$	Free path for non-thermal neutrons $= 5\lambda_0$
$\frac{\text{Number of thermal neutrons}}{\text{Number of non-thermal neutrons}}$ Inside	80	16
$\frac{\text{Flux of thermal neutrons}}{\text{Flux of non-thermal neutrons}}$ Inside	5	1
$\frac{\text{Flux of thermal neutrons}}{\text{Flux of non-thermal neutrons}}$ Outside	2	$\frac{1}{6}$
$\frac{\text{Flux of thermal neutrons inside}}{\text{Flux of thermal neutrons outside}}$	8	20
$\frac{\text{Flux of non-thermal neutrons inside}}{\text{Flux of non-thermal neutrons outside}}$	3	$2\frac{1}{2}$

§ 6. COMPARISON WITH EXPERIMENT

(i) A piece of silver foil was placed on the surface of a large block of wax, a source of fast neutrons being placed outside the block in the plane of the surface, figure 1. After a known period of irradiation, the foil was removed and its β-ray activity was measured. The experiment was repeated with a second block of wax, identical with the first, lying on the top of the foil, which was thus at the centre of the composite block. The activity in the second case was greater in the ratio of (13 ± 2) to 1. This lies about midway between the two values 8 and 20 given in table 2 for the inside : outside flux ratio for thermal neutrons, and is higher than either of the two values 3 and $2\frac{1}{2}$ given for non-thermal neutrons. The activity obtained within the block is known to be very largely due to thermal neutrons; see (ii) below. Calculation and experiment agree if it be assumed that thermal neutrons are also mainly responsible for the activity of a specimen of silver exposed outside the block.

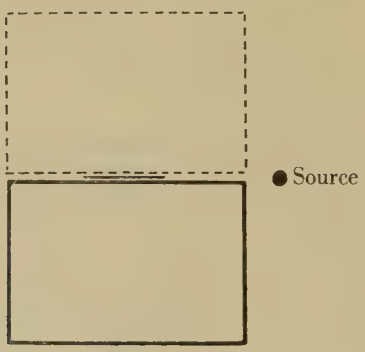

Figure 1.

(ii) If a change be made in the temperature of the walls of a cavity in a large block of wax, the thermal neutrons passing through the cavity have an altered velocity-distribution, and there is a corresponding change in the amount of radio-activity which the neutrons produce in a thin specimen of (for example) silver exposed within the cavity[4]. When the walls are cooled from the temperature of the room to that of liquid oxygen, the change in activity may be as much as 35 per cent for silver, and 50 per cent for copper; it follows that a large fraction of the activity is due to thermal neutrons. When, however, the temperature of the outside of the block is altered, very little change can be observed in the activity of a specimen exposed to the emergent neutrons, although experiments with revolving discs have indicated that some, at least, of the neutrons have thermal velocities[5]. A possible explanation would be that the proportion of thermal neutrons outside a block of wax is actually much less than inside, and constitutes only a very small fraction of the emergent flux, but the present calculations show this to be unlikely. It seems possible that a cold layer at the surface of a block is comparatively ineffective for changing the velocity-distribution of warm neutrons passing through it; an experi-

mental confirmation of this suggestion is described by Mr J. R. Tillman in an accompanying paper[6]. The superior efficiency of a thin-walled enclosure as compared with a single cold layer must be due to the scattering back into the enclosure of neutrons which have already made one transit through the cold wall.

REFERENCES

(1) Bjerge and Westcott. *Proc. roy. Soc.* A, **150**, 709 (1935).
(2) Frisch and Placzek. *Nature*, Lond., Feb. 29th (1936).
(3) Amaldi, d'Agostino, Fermi, Pontecorvo, Rasetti and Segrè. *Proc. roy. Soc.* A, **149**, 522 (1935).
(4) Moon and Tillman. *Proc. roy. Soc.* A, **153**, 476 (1936).
(5) Dunning, Pegram, Fink, Mitchell and Segrè. *Phys. Rev.* **48**, 704 (1935).
(6) Tillman. Page 642 of this volume.

539.185

NOTE ON THE NEUTRALITY OF THE NEUTRON

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Received April 6, 1936. *Read June* 5, 1936

ABSTRACT. From the lack of influence of an electric field upon neutrons of thermal velocities it is shown that the neutron has no electric charge so great as 10^{-7} of the electronic charge.

Dr E. C. BULLARD remarked to me recently that some interest might lie in an extremely accurate experimental proof that the neutron is free from electric charge. Chadwick's original proof that neutrons are unaffected by electric fields was made with fast neutrons; now that neutrons having thermal energies are available the sensitivity of such a test can be very greatly increased.

For this purpose I exposed a specimen of silver within a cavity in a large wax block through which neutrons were passing. The resulting β-ray activity was measured, and the experiment was then repeated with the silver at a potential of $+50{,}000$ volts with respect to the wax, and again with the silver at a potential of $-50{,}000$ volts. In no case was there a detectable difference in the observed activity.

Since the majority of the neutrons had kinetic energies of the order of 0·03 electron-volt, a charge of $6 \times 10^{-7}e$ would have prevented them from passing through an opposing potential difference of 50,000 volts, and one-sixth of this charge would have entailed a detectable difference between the observed activities. It is to be concluded that the neutron possesses no charge so great as 10^{-7} that of the electron.

534·5·07

EXPERIMENTS WITH A NEW TYPE OF RIPPLE TANK

By E. TYLER, D.Sc., M.Sc., F.Inst.P., Department of Physics, The College of Technology, Leicester

Demonstration given on March 20, 1936

§ 1. INTRODUCTION

In large-scale ripple-tank work it is customary to demonstrate first with single-pulse disturbances, examining them as they recede from the source. The time of viewing any particular wave is usually short, so that the effects are quickly lost to the observer. It is therefore advantageous to extend the demonstrations to unlimited wave trains and to view the resultant effects stroboscopically. In view of the limited accommodation in most teaching institutions and the relatively high cost of most of the commercial types of projection ripple tanks, an attempt has been made to overcome these drawbacks.

§ 2. TECHNIQUE AND FORM OF APPARATUS

Designed primarily for lecture demonstrations in rooms of medium size, the apparatus is intended to satisfy the following requirements. (*a*) It must be capable of being operated from either a.-c. or d.-c. mains under synchronous conditions or otherwise. (*b*) It must be self-contained and portable with easy adjustments. (*c*) Demonstrations with mercury and water ripples in daylight as well as in a dark room must be possible. (*d*) It must be adaptable for use with modern discharge tubes operated from the a.-c. mains.

For general work the apparatus functions as an autolamp synchronous dual-reed device controlled by the a.-c. mains supply at 50 c./sec. and 100 or 200 V. The addition of a small motor of variable but controlled speed to drive a slotted disc acting as an interrupter, together with a contact breaker actuating the rippler, increases the utility of the apparatus, since means are thus provided for demonstrating progressive waves, in addition to stationary patterns at various frequencies.

The lay-out of the apparatus is shown in figure 1, and a schematic arrangement of the possible methods of use in figure 2.

The apparatus is mounted on two boards A and B, the former being mounted vertically on the latter. A carries the major components of the equipment, and B, the ripple tank C, a levelling table D, and rippler R_2.

For the autolamp dual-reed method the availability of the a.-c. mains is essential to operate two independent reeds R_1 and R_2 in series. R_1 functions as an interrupter cutting off intermittently from the ripple tank the light emitted by a 60-watt auto-

lamp. R_2 carries the necessary iron dippers and so produces ripples in synchron-
zation with the intermittent illumination.

The autolamp is enclosed in a lamp-house mounted on an arm G. Variou
movements are thus possible for effecting adjustment of the lamp position, whic
must be such that an image of the lamp filament is formed horizontally an

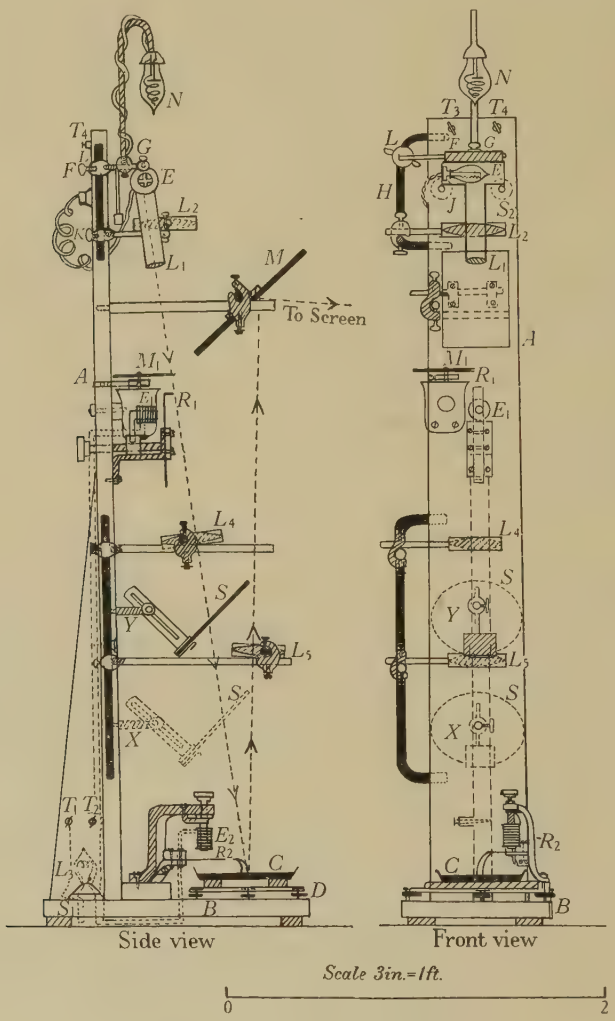

Figure 1. Mounted form of ripple tank.

coincident with the bent end of the reed R_1. This ensures sharp cut-off in the
illumination. Both reeds are actuated by electromagnets E_1 and E_2 in series with
the a.-c. mains supply, and for control of the current passing through these coils
(each consisting of 800 turns) a 100-watt lamp is also included in the circuit
together with a controlling switch S_1. The supply voltage is connected to T_1 and T_2.
It is essential to operate R_1 at resonance with the mains, but R_2 need not be driven

such a condition. Provision is also made for varying the air gaps between the reeds and the electromagnets and so effecting control of the amplitudes of the reeds. Whereas R_2 vibrates at a very small amplitude, R_1 vibrates with amplitudes ranging up to 1 cm. The ripple tank consists of a half-plate photographic developing dish, and for water ripples it is preferable to have a plane mirror in the bottom.

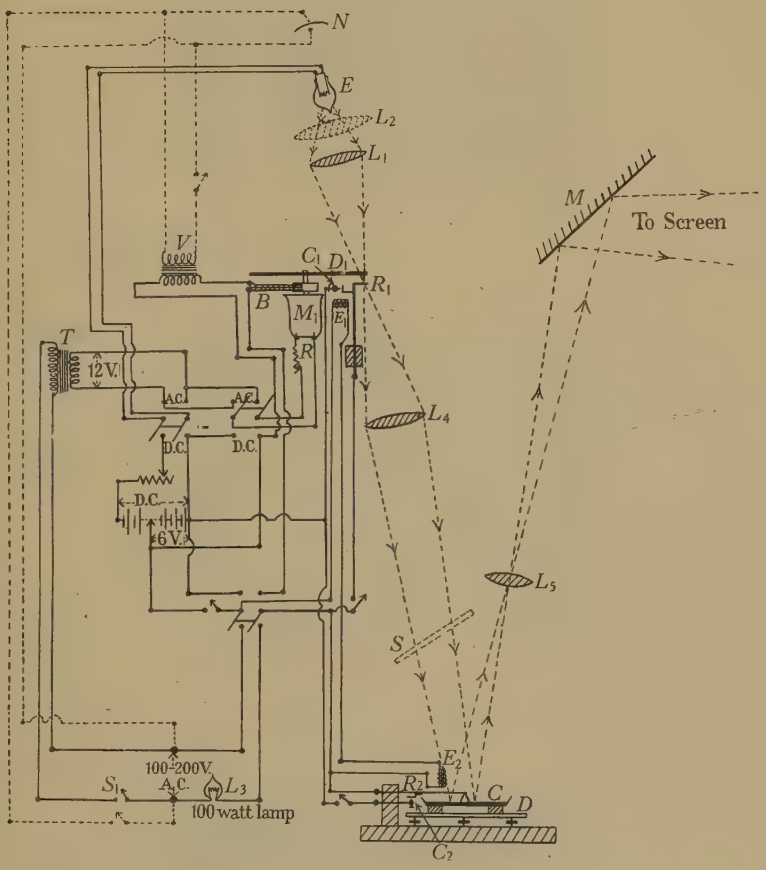

Figure 2. Schematic arrangement showing possible methods of operating ripple tank. E, auto-lamp; N, neon lamp or discharge tube; R_1, interrupting reed; E_1, E_2, electromagnets; R_2, ripple vibrator; L_1, focusing lens ($f=7{\cdot}5$ cm.); L_4, L_5, focusing and projecting lenses ($f=30$ cm.); M, plane mirror; C, ripple tank; M_1, motor driving slotted disc; D, levelling table; S, ground glass screen; T, transformer; B, contact-breaker; C_1, C_2, reed contacts.

By being placed on two pieces of rubber sponge fixed on a levelling table, the tank can be freed from any extraneous vibrations that may arise from possible forced vibrations of the apparatus resulting from vibration of the reeds. Further sound-insulation is effected by using rubber washers between the baseboard and the metal framework carrying R_2. Projection of the ripple images is effected by means of the lenses L_4 and L_5 and mirror M. At a distance of 3 or 4 metres a picture about 3 ft. square is easily obtained with good illumination.

In order to demonstrate progressive waves and the apparent slowing up of th ripples a small motor M_1 (either a.c. or d.c.) is used to drive a slotted disc havin four equally spaced radially slots. This disc is mounted alongside R_1 and takes it place for showing progressive waves. A contact-breaker also is attached to th spindle of the motor enabling the equipment to be operated from a d.-c. supply as well as by a.-c., in addition to permitting demonstrations at frequencies othe than that of the a.-c. mains. Pieces of watch spring bent to the desired curvatur function as reflectors.

The adoption of modern discharge tubes as stroboscopic illuminants in th place of the autolamp only allows for close-up viewing of the ripples, either directly on the ripple surface or via the mirror M. The experiments must in this case be performed in a dark room and the reed R_1 dispensed with. The Osglim lamp is perhaps the most convenient and simplest discharge tube to use, especially when operated from the 200-V. a.-c. supply. Such a lamp is mounted at N and light from it is focused on the ripple surface by means of the lens L_2. Synchronization is thus automatically effected between the intermittent illumination and the ripple-formation. The upper terminals T_3 and T_4, socket J, and switch S_2 are all in series with the 200-V. a.-c. mains, the latter being applied to T_3 and T_4. The plug connecting the Osglim lamp is placed in the socket so that when S_2 is closed the neon lamp flashes at 100 flashes per second. This arrangement of terminals, socket, and switch all in series is readily adaptable to either type of lamp and power-supply. When other discharge tubes are used in place of the Osglim lamp, they are either mounted above the tank or placed at some distance from it on a level with the position occupied by the neon lamp; then light from the discharge tube is reflected by an inclined mirror on the vertical arm down via the lens on to the ripple surface so as to give stroboscopic effects automatically. These discharge-tube methods usually provide for only one length of ripple, but a wider range of frequencies can be attained by the neon lamp, substituting for R_2 a loudspeaker unit carrying the dippers, and operating both it and the neon lamp simultaneously from either a valve oscillator, an oscillating neon tube, a contact-breaker and transformer device, or a thyratron relay source, all of controlled but variable frequency.

§ 3. INSTRUCTIONS FOR METHODS OF OPERATING THE TANK WITH A.-C. MAINS SUPPLY ONLY, AT 100–200 V., AT 50 C./SEC.

(i) For viewing or projecting the stationary patterns at mains frequency, use an autolamp source E, and electrically maintain both reeds R_1 and R_2 by energizing the electromagnets E_1 and E_2 in series with lamp L_3 and the a.-c. supply.

(ii) For viewing directly through the mirror M, and with either a neon-lamp source or some other discharge tube, dispense with reed R_1 as chopper, and operate both the reed R_2 and the lamp source from the 200-V. a.-c. supply, the lamp L_3 again being in series with R_2.

(iii) To distinguish between progressive and apparently stationary ripples, use the motor M_1 and a 6–12-V. a.-c. supply from transformer T, figure 2, and rotate

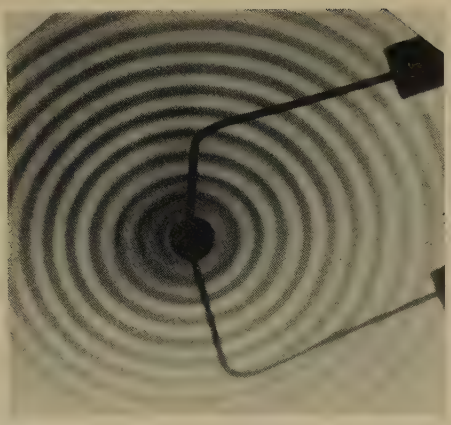

Figure 3. Circular waves in water. Exposure 4 sec. auto-lamp reed method.

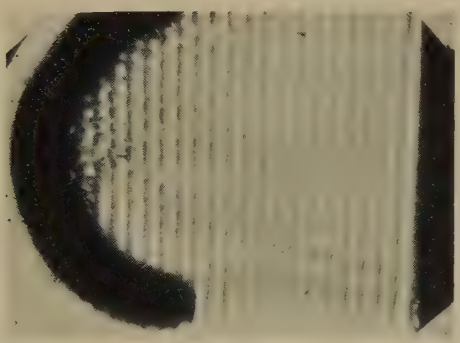

Figure 4. Reflection of plane waves at a concave barrier in mercury. Exposure 1 sec. auto-lamp reed method.

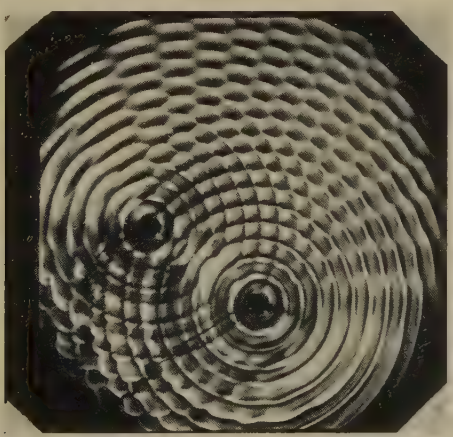

Figure 5. Interference in mercury. B.T.H. neon tube. Exposure 30 sec.

To face page 662

sc D_1, which has four slots, rendering the light from the autolamp intermittent fore it falls on the ripple tank. Simultaneously maintain the rippler R_2 by means a.-c. supply fed through lamp L_3, speed-control of the disc being effected with riable resistance R.

(iv) To demonstrate at correct stroboscopic conditions for different frequencies a.c., drive the motor from a 6 to 12-V. a.-c. supply, and use the contact-breaker in series with a 6-V. d.-c. supply and electromagnet E_2 to actuate the rippler R_2. ne number of contacts on the spindle is the same as the number of slots in the sc per revolution.

§ 4. INSTRUCTIONS FOR METHODS OF OPERATING WITH D.-C. SUPPLY AT 6–12 V.

(v) Use the autolamp source at 12 V.; electrically maintain R_1 by means of and contact C_1, and drive R_2 in synchronization with it. E_1 is in series with E_2. ake R_1 function as an interrupter as in method (i). Only one frequency is obtain- le, viz. that of R_1.

(vi) To distinguish between progressive and stationary ripples using an auto- mp source, maintain R_2 electrically by means of the contact C_2 and a 6-V. supply, d at the same time run the motor at a variable speed so as to drive the slotted sc functioning as the light interrupter.

(vii) For obtaining synchronous effects at all frequencies on d.-c. supply, employ tolamp E, rotating disc D_1 driven by motor M_1, and the contact-breaker B, the ter being in series with the electromagnet E_2. R_2 is thus actuated at frequencies ual to that of the make-and-break current at B. The frequency of ripple-formation thus controlled by the speed of the motor.

(viii) With the neon-lamp source and for synchronous conditions at all fre- encies, couple the lamp to the circuit containing R_2 the rippler and the contact- eaker at B by means of the transformer V. The flashing frequency of the neon mp is then the same as that of the rippler at all speeds of the motor. A 6-V. d.-c. pply is sufficient in this case.

(ix) For working at a fixed frequency, maintain R_2 electrically by its own make- d-break contact or drive it by R_1, still using the make-and-break method. At e same time couple the neon lamp to this circuit as in method (viii).

(x) To distinguish between progressive and stationary ripples with a neon- mp source, operate R_2 as in method (ix), running the motor at the same time to tuate the contact-breaker B, which causes the neon lamp to flash at a rate equal that of the make-and-break. By speeding up the motor the flashing may be ought slowly into synchronization with the ripple-formation.

§ 5. SPECIMEN PHOTOGRAPHIC RESULTS

These are shown in figures 3, 4 and 5. Figures 3 and 4 are typical results for ater and mercury obtained by the autolamp dual-reed method, and figure 5 ows the type of result obtainable with the recently developed B.T.H. strobo-

scopic discharge tube. Imperial Process Eclipse plates, speed 650, give satisfactory results.

The illumination provided by other discharge tubes such as the Osira mercury street-lighting, Osira sodium, and neon sign, fluctuate sufficiently in intensity to give reasonably good stroboscopic effects[1]. The cut-off in illumination with all these types of lamps is not so sharp as with either the autolamp or B.T.H. tube. The duration of the flash for each half-cycle of excitation is relatively long also. These effects thus render the definition of the ripple images not so good as those obtained with the autolamp reed device and the B.T.H. tube.

The advantage possessed by the B.T.H. tube as a stroboscopic illuminant is most outstanding and convincing. Owing to the relatively large amount of light available, the adaptation of such a lamp to large-scale ripple-tank work seems highly favourable.

§ 6. ACKNOWLEDGMENTS

My thanks are extended to the B.T.H. Co., Rugby, for loaning me the stroboscopic discharge tube; also to their research staff for the kindly interest taken in this section of the work.

REFERENCE

(1) Tyler. *School Science Review*, **17**, June (1936).

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THE MAGNETIC PROPERTIES OF MANGANESE HEATED IN NITROGEN

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AND

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ABSTRACT. The combination of amorphous manganese with nitrogen has been studied over the temperature range 300–1000° C., and it has been found that ferromagnetic compounds are formed at much lower temperatures than had been reported previously. The magnetic hysteresis phenomena exhibited by these compounds have been studied, and their ferromagnetic Curie points have been determined by a simple method. An X-ray study of their structures has also been made; it is found that the existence of ferromagnetism can be associated with a γ phase of manganese with a slightly enlarged lattice constant; the function of the nitrogen is not completely understood.

§ 1. INTRODUCTION

During an investigation of magnetic properties of amorphous manganese Bates and Reddi Pantulu[1] observed that some of the specimens exhibited traces of ferromagnetism when the amalgams from which they were prepared had been in contact with air for a longer time than was desirable. Manganese specimens made under the best conditions were definitely paramagnetic and did not show any traces of ferromagnetism. It is well known that manganese readily combines with many non-magnetic elements to give ferromagnetic substances, and it appeared likely that some of the manganese used in these experiments had combined with atmospheric nitrogen.

In 1909 Wedekind[2] obtained three nitrides of manganese, Mn_3N_2, Mn_5N_2, Mn_7N_2, prepared at various temperatures between red heat and that of the oxyhydrogen flame; he found that the higher nitrides were strongly magnetic and the lower nitrides feebly magnetic. Later, Ishiwara[3] used Kahlbaum manganese and suggested that manganese formed two compounds and a solid solution with nitrogen in the temperature interval 600–1600° C. All three were found to be ferromagnetic and were distinguished by their thermomagnetic properties and their Curie points T_f, which are given in table 1.

More recently Ochsenfeld[4] has made magnetic and X-ray studies of the manganese-nitrogen compounds obtained by heating manganese in nitrogen at 1100° C. and he has attributed the observed ferromagnetism to the solution of nitrogen in the γ phase of manganese. The lattice constant and the intensity of magnetization increased with increase in nitrogen concentration. Ochsenfeld obtained an atomic

concentration of as much as 12 per cent and found the lattice constant to be increased from 3·80 to 3·86 A., while the maximum value of the intensity of magnetization was about 40 c.g.s. units. He found the Curie point for one typical specimen to be 500° C., its coercive force H_c at room-temperature being 200 oersteds. He was unable to obtain magnetic saturation even with fields of 650 oersteds; in

H_c

Table 1

Compound	Preparation	Curie point T_f
Mn_3N_2	Heated in nitrogen from 1200 to 1600° C.	One at 50° C. One at 750° C.
Mn_5N_2	Heated in nitrogen from 600 to 1300° C.	500° C.
Mn_7N_2	Heated in NH_3 at 1450° C.	750° C.

his experiments the demagnetizing factor was negligibly small. An X-ray study of a large number of specimens, prepared by heating finely powdered Geyler manganese to a high temperature in a stream of ammonia or nitrogen, has been made by Hägg[5]. He found that the specimens so prepared were not homogeneous, and they were therefore maintained for some days at a temperature of 400 or 600° C. in an evacuated sealed tube to make them homogeneous.

It will thus be seen that all the previous investigators studied the behaviour of compounds of manganese and nitrogen prepared at high temperatures only. It is equally important to know whether ferromagnetic compounds can be formed at relatively low temperatures. Accordingly the following experiments were carried out, and have provided much additional information concerning the temperature range 300–1000° C.

§ 2. PREPARATION OF SPECIMENS

Manganese amalgam was prepared by electrolysis in the manner previously described[4]. It was quickly transferred from the bath to the pyrex glass apparatus shown in figure 1, which was then evacuated and heated to 300° C. to drive off the mercury, which was condensed and collected in a water cooled bulb. After most of the mercury vapour had been driven off, a mercury pump and liquid-air trap were used to remove the last traces. The water-cooled bulb was then sealed at a constriction and removed. A three-way tap connected the pyrex apparatus either to a hyvac pump or to a nitrogen cylinder. The nitrogen was first passed over heated copper filings, to remove any oxygen present, and then through condensers surrounded by water and liquid air, respectively, to remove water vapour. A simple mercury barometer tube was used in the nitrogen circuit to act as a safety valve and also as a pressure-indicator.

Specimens were prepared by allowing the purified nitrogen to remain in contact with manganese maintained at chosen temperatures, 300, 400, 500 and 550° C. for an hour in each case, after which the manganese was allowed to cool slowly in contact with nitrogen. Some of the compounds thus formed were forced into one

of the small tubes, the pyrex glass beads in the apparatus being used for this purpose. The apparatus was then evacuated and the filled tube was sealed and detached. The remaining manganese was heated anew in the presence of nitrogen and kept at another higher fixed temperature for 1 hour, the whole procedure being repeated until all the tubes were filled. For specimens treated at higher temperatures, 750, 800, 900 and 1000° C., a quartz apparatus similar to the pyrex apparatus of figure 1 was used.

§3. MAGNETIC EXPERIMENTS

The Gouy method for the investigation of the magnetic properties of these specimens was successfully used in the case of that treated at 300° C. Some of the remaining specimens were so ferromagnetic that lateral displacements made such measurements impossible, and consequently a ballistic method was employed. A water-cooled solenoid with eight layers, each of 302 turns, was used as the magnetizing solenoid. Two equal coils of double-silk-covered wire, s.w.g. 36, were wound on similar ebonite formers. These were placed axially inside the solenoid and connected in opposition so that on reversal of the current in the solenoid only a small deflection was observed with a ballistic galvanometer connected to the coils. One of the coils was placed in the middle of the solenoid and the other some 5 cm. below it. A smaller compensating coil in series with the first two was used for fine adjustment to give complete compensation when a current of 10 amperes was reversed in the solenoid. The magnetizing solenoid was supplied from a 120-volt battery of accumulators, and suitable resistances by which the current could be reduced in steps from 10 amperes were used. The specimen under examination was placed in the ebonite coil in the middle of the magnetizing solenoid, and the hysteresis cycle was obtained in the usual way by observing the throw of a ballistic galvanometer for known changes of current.

In order to calibrate the ballistic throw in terms of the induction in the specimen, a test solenoid of 200 turns was wound on a glass tube 6·2 cm. long, of the same diameter as the specimen, and placed in the region formerly occupied by the latter. A known current was then reversed through this test solenoid and thus the deflection of the galvanometer corresponding to the reversal of a known number of lines could be observed. In order to take account of the packing density of the specimens, the specific magnetization or magnetic moment per gram was found by making the appropriate weighings in each case.

The ferromagnetic Curie points of the specimens were determined by a very simple method; the necessary apparatus is shown in figure 2. A thick-walled copper tube was coated inside and out with Insulate cement and wound non-inductively with two layers of nichrome strip, the successive layers being insulated by the same cement. The furnace was provided with a quartz side tube *P*, and with circular end pieces of asbestos furnished with mica windows. A thermocouple *Th* was used to measure the temperature of the furnace. The latter was placed directly above the poles of an electromagnet cooled by passing water through the metal tubing *pp*.

Over *P* was slipped the tube *Q* which carried the torsion head *T*. From *T* a

long and stiff quartz fibre was suspended from a short length of weak phosphor bronze strip. A sample of a compound was packed and sealed inside a quartz tube about 3 cm. long and 2 mm. in internal diameter. The tube and its contents were provided with a thin platinum wire loop which was hooked on to the end of the quartz fibre. The loop was rigidly connected to the quartz tube and to the quartz hook by Insulate cement. The suspended system was then given a preliminary heating to cause the cement to set hard.

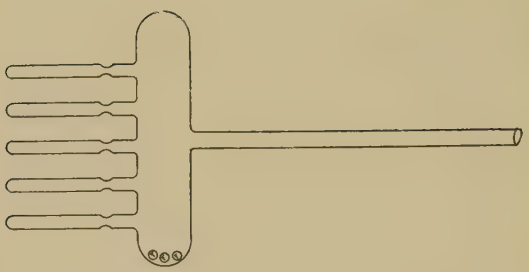

Figure 1. Apparatus for preparation of specimens.

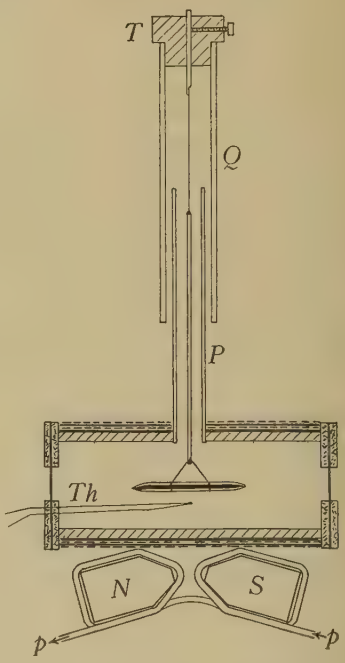

Figure 2. Apparatus for determination of Curie points.

The magnet was excited by a current of 5 A., causing the specimen to be magnetized strongly. The current was then reduced to 0·5 A., sufficient to provide a constant field of some 125 oersteds in which the specimen was made to oscillate. Since the phosphor-bronze suspension was very weak, the reciprocal of the square t of the period t of oscillation was almost directly proportional to the product of the magnetic moment and the applied field. A series of values of the period of oscillation were obtained at different temperatures under these conditions. The curves obtained by plotting $1/t^2$ against the corresponding furnace temperatures are shown in figure 3, arbitrary units being used to give a common axis. The very marked changes in $1/t^2$ enables us readily to fix the Curie points with a degree of accuracy sufficient for the present work. The provision of the long quartz fibre ensured that the torsion constant of the suspension should not appreciably change with furnace temperature, and these arrangements were very satisfactory indeed up to temperatures of 600° C. This is well shown by the curve labelled Ni in figure 3 which represents the curve obtained when a pure nickel rod, 3 cm. long, was placed inside a quartz tube and used as a specimen. In this case a field of some 50 oersted

as employed in the measurement of t. The Curie point obtained from this curve 354° C., which compares favourably with the accepted value $356 \pm 2°$ C.

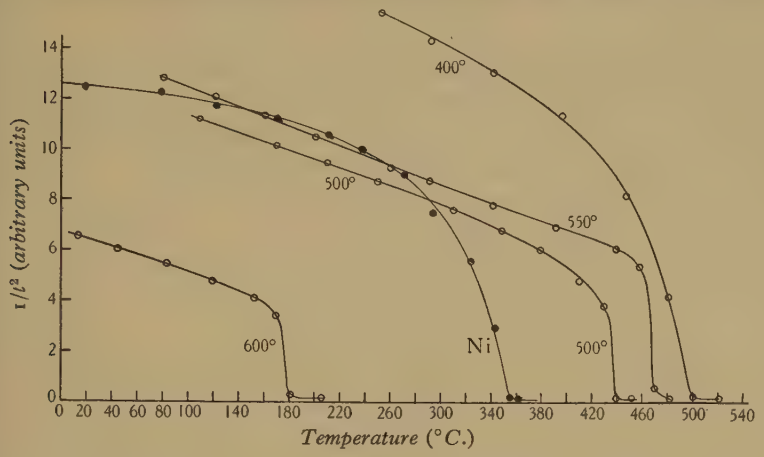

Figure 3. Curves for determination of Curie points. ○ manganese heated in nitrogen; ● nickel for comparison.

§4. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the Gouy measurements of the specimen prepared at 300° C. ave a linear variation of k with $1/H$, showing clearly that a small but definite mount of ferromagnetism existed. It is felt that although this might have been creased with longer time of preparation, it is so small that the possibility of its eing due to a trace of iron impurity cannot be excluded. Hysteresis curves were btained for the specimens prepared at 400, 500, 550, 600° C., but it was impossible o obtain curves for the remaining specimens. The curve for the specimen prepared 400° C. is shown in figure 4, where the intensity of magnetization per gram is lotted against the applied field. No correction was made for demagnetization ctor, for although the pyrex tubes were of internal diameters 0·44, 0·45, 0·44, 0·48, ·36 cm., the observed intensity of magnetization was in every case too small to arrant the application of such correction. The relevant data are given in table 2.

Table 2

Temperature during preparation (° C.)	300	400	500	550	600
Coercive force (oersteds)	—	153·4	109·6	116·9	73·0
Specific magnetization in a field of 730 oersteds	$(0{\cdot}7\times10^{-3})$	6·98	8·76	9·49	1·21
Ferromagnetic Curie point (° C.)	—	500	430	470	182

On comparing these hysteresis curves it was seen that in all cases magnetic aturation was not obtained even for a field of 730 oersteds, and there were pro-ressive differences in the maximum values acquired in that field and in the oercive forces, as recorded in the above table. The specimens prepared at higher

temperatures of 700–900° C. in the quartz tubes showed no measurable magnetization when tested by the ballistic method, in spite of the fact that these specimens were allowed to cool slowly in contact with nitrogen. Ochsenfeld found that Geyler manganese took up nitrogen in considerable quantities at 1060° C. but re-emitted it at temperatures between 1300 and 1320° C. The hysteresis curve obtained for one of his specimens prepared between these temperatures was remarkably similar to the curves obtained by us; saturation was not reached at 650 oersteds, and the coercive force was 200 oersteds, a value somewhat higher than that obtained with our preparations.

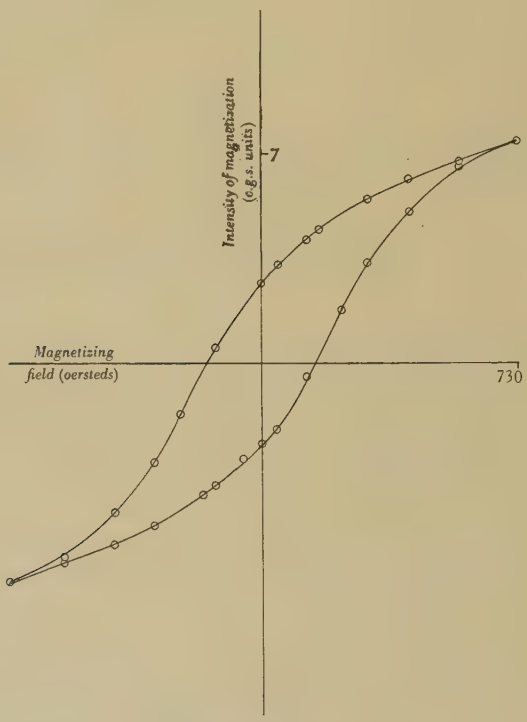

Figure 4. Hysteresis curve for specimen of manganese heated in nitrogen at 400°.

X-ray photographs were taken of the samples of amorphous manganese heated respectively to temperatures of about 300, 400, 500, 550, 600 and 1000° C. in contact with nitrogen. The powders were enclosed in very thin tubes of Lindemann glass and photographed with copper rays by means of a circular camera. A visual comparison of the photographs clearly revealed the existence of structural differences between the specimens, in fact, the photographs fall into three groups; the first comprises only that of the 300°-C. specimen, the 400, 500 and 550°-C. specimens account for the second group, whilst the photographs of the 600 and 1000°-C. specimens have been allocated to the third group. Each group contains photographs either exactly alike or very similar, but differing markedly from those of other groups. Such a division amongst the specimens is in general agreement with the magnetic observations, according to which the second group contains just those

ecimens which exhibit ferromagnetic properties to the greatest extent. Further notographs will be taken later with a more suitable apparatus to attain a greater easure of accuracy, as that in use was not of the design best suited to this type of ecimen.

The results of each photograph will be discussed in turn, beginning with that ferring to the lowest-temperature specimen. This photograph is representative of simple cubic structure of cube-edge 6·28 A., corresponding therefore to manganese in its β phase; no γ phase lines were visible. All photographs of the second oup of specimens exhibited a superposition of two structures, the simple cubic rresponding to the β phase of manganese already mentioned, together with a ce-centred cubic structure allied possibly to the face-centred tetragonal cell of the phase of manganese. Considering firstly the simple cubic structure of the β phase, e cell-size appears to have increased slightly to 6·38 A. for all these specimens; e reflections arising from this are all very weak. On the other hand the γ phase strongly marked and gives rise to the reflections (111) st., (200) st., (220) st., 311) v.st., (222) m/w, (331) w, and (420) w; the cell-size is 3·84 for the 400°-C. ecimen and 3·86 for the 500 and 550°-C. specimens. These values are similar those found by Ochsenfeld for specimens treated at much higher temperatures d exhibiting grating-sizes large compared with the non-magnetic nitrogen-free phase of manganese, and correspond to some extent with the results of Hägg r what he terms the ϵ phase.

The outstanding feature of the photographs of the last group, comprising the oo and 1000°-C. specimens, is their much greater complexity and the general eakness of the lines; to permit of interpretation, they need the higher accuracy view. The photographs, though differing in detail, show a marked similarity to ne another. They differ entirely from those of previous groups and do not show any ace of the enlarged γ phase; this is of interest particularly as far as the 600°-C. ecimen is concerned, for this still displays ferromagnetic properties; longer xposures will disclose whether this phase is entirely absent.

It is clear that the behaviour of manganese in contact with nitrogen presents a roblem of some complexity. The present study shows that finely divided manganese eacts far more readily at comparatively low temperatures to form ferromagnetic ubstances than was previously believed. The function of the nitrogen cannot be educed from the X-ray observations, although the expansion of the lattice suggests hat the nitrogen acts merely by separating manganese atoms without forming a efinite chemical compound. The experiments with the 300°-C. specimen definitely uggests that the ferromagnetic impurity in this case is iron introduced during the lectrolysis, and provides additional evidence for the view that pure manganese is ot ferromagnetic.

REFERENCES

(1) Bates, L. F. and Reddi Pantulu, D. V. *Proc. phys. Soc.* **47**, 197 (1935).
(2) Wedekind, E. *Ber. dtsch. chem. Ges.* **41**, 3769 (1908); **46**, 3763 (1913).
(3) Ishiwara, T. *Sci. Rep. Tôhoku Univ.* **5**, 53 (1916).
(4) Ochsenfeld, R. *Ann. Phys.*, Lpz., **12**, 353 (1932).
(5) Hägg, G. *Z. phys. Chem.* B, **4**, 346 (1929).

REVIEWS OF BOOKS

Molekülstruktur, von Dr H. A. Stuart, Struktur und Eigenschaften der Materie, XIV. Pp. x+388. (Berlin: Julius Springer.) RM. 32.

Quantenmechanik der Materie und Strahlung, *Handbuch d. Radiologie*, Band VI, 2 Auflage, Teil II: *Moleküle*. (Leipzig: Akademische Verlagsgesellschaft.) RM. 54.

There have been great advances in our knowledge of the structure of molecules during the last few years owing to the discovery of new experimental methods of attack. The diffraction of X rays and of electrons by molecules has been used to determine the disposition of individual atoms in molecules, Raman spectra and infra-red spectra have yielded information as to the internal vibrations of these atoms in relation to one another, and in some cases measurements of dipole moments have been used to infer the degree of relative motion of groups within a molecule. In view of these advances in so many different but related fields it is useful to have a connected account of the information now available as to the structure of molecules, and nowhere can a better or more complete summary of these advances be found than in the book by H. A. Stuart.

After a brief review of present theories of the forces which hold molecules together, of modern theories of valency and of the new conception of the nature of single and double bonds, the author goes on to describe methods of determining the outer forces which molecules exert on one another. From the external properties he passes to the internal properties and gives experimental details of methods of registering the scattering of X rays and electrons by gases, ending with a summary of the internal dimensions of a number of inorganic and organic molecules obtained by such methods.

There is an authoritative account of methods of determining dipole moments, as would be expected of an acknowledged expert in that field. The chemist interested in stereochemistry will find the discussion of the structure and internal motion of molecular groups most informative.

The optical properties of molecules as indicated by the Kerr and other effects are described at considerable length—probably at too great length, seeing that most of the work described is classical and has been dealt with adequately many times. The second half of the book is concerned mainly with the vibrations of molecules and with the methods by which they are determined and assigned. The selection rules of infra-red spectra and Raman spectra are given, and the characteristic features of these two complementary methods are summarized. Details of a large number of simple and polyatomic molecules are recorded and altogether this section is extremely useful for purposes of reference. The book concludes with tables of the size, structure, fundamental frequency and other properties of diatomic, triatomic and polyatomic molecules.

The reviewer can confidently recommend Dr Stuart's book as a clear, reliable account of an important subject. It is profusely illustrated, contains comprehensive references to the literature, and bears the signs of a careful and thorough piece of work.

The other book under review consists of a series of articles by experts on the properties of molecules. It covers very much the same ground as the book by Dr Stuart but the accounts of the separate subjects, while more detailed and technical, are less coordinated than his. The theory of molecular spectra is given in a general, non-mathematical way by R. de L. Kronig, who deals with the quantum numbers and method of description of rotational, vibrational and electronic states. This leads him to a discussion of predissociation and other related phenomena associated with molecular spectra.

There is an authoritative article by P. Debye and H. Sack on the electrical properties of molecules such as induced polarizabilities, dipole moments, and the effect of these on

spersion in gases and fluids, together with a learned discussion of the Raman effect by . Placzek (pp. 209–374). This is the most complete and thorough discussion of the eory of Raman scattering that the reviewer has seen, for it contains an account of the mmetry properties of molecules and of the selection rules for each class of symmetry, nich is nowhere else accessible.

Dr F. Block contributes an article on the molecular theory of magnetism with sections the diamagnetism and paramagnetism of atoms and molecules and the ferromagnetism the iron group of solids. The quantum theory of valency is dealt with by W. Heitler. ter describing the quantum numbers of atoms and molecules, he develops the theory of e interaction of unsaturated atoms and shows the importance of spin in determining the agnitude of the forces between atoms. This article was, however, completed some time fore publication and some of the later developments of the theory are not included.

The present volume, containing as it does a number of scholarly articles by well-known thorities, worthily maintains the standard set in earlier volumes of the Handbook and ll be welcomed by all those interested in the rapidly growing subject of molecular ucture.

J. E. L.-J.

isibility in Meteorology. The Theory and Practice of the Measurement of the Visual Range, by W. E. KNOWLES MIDDLETON, Toronto. Pp. viii + 104. (Oxford University Press and The University of Toronto Press, 1935.) 8*s*. 6*d*. net.

"Stultus est qui fructus magnarum arborum spectat, altitudinem non metitur." These rds apply to no science more fitly than to visibility; indeed it would not be exaggerating say that the usefulness of visibility statistics, if not the very science of forecasting sibility, has been seriously hampered by the lack of precise methods of measurement sed upon a clear understanding of the different forms and aspects of visibility and their lations. Yet this book is the first to co-ordinate and review the all-too-small amount of st work on the subject. The author has not merely filled a gap in our literature, he has oduced a readable and comprehensive book, of value both to the general reader and to e specialist.

The accounts given of past researches are clear, concise and reliable. The elucidation the subject is, however, so incomplete, and the question "What are the best means of easuring visibility" is so controversial, that it is only to be expected that views should casionally be expressed which can only be regarded as personal and not generally tablished. It is in no carping spirit that it is pointed out that the author's views on a rational scale of visual ranges" will probably not be acceptable to many persons terested from points of view different from that of the author. Nevertheless, the avowed rposes of the book—"to put measurements of visual range on a more rational basis, to prove the techniques of observation, and to stimulate investigation"—are well served.

M. G. B.

he Revolution in Physics, by ERNEST ZIMMER. Translated by H. S. HATFIELD. Pp. xiv + 240. (London: Faber and Faber, Ltd.) 12*s*. 6*d*. net.

That part of the science of physics which deals with fundamental entities, their natures nd their interactions, is growing very rapidly and is of great interest to scientist and to yman. This excellent survey of the experimental discoveries and of the theories accom- anying them is a welcome addition to the immense body of literature on physics. The eatment throughout the book is non-mathematical and, while details of experimental chnique are purposely omitted, the diagrams and photographs supplied are sufficient indicate clearly the general nature of the evidence on which modern views are based.

After some discussion of the nature of matter and light according to classical physics,

the reader is presented with an account of the quantum hypothesis and its application in the study of the structure of atoms. The necessity for the introduction of new ideas and assumptions is made very clear and the subsequent developments of the wave theory which have led to the present-day conceptions of a wave-model atom are lucidly described.

The last chapter on "Science and philosophy" indicates how the new physics offers some contribution towards the solution of problems which have stirred the thoughts of philosophers throughout the ages. The position to-day may be summarized by such quotations as "the world is more mysterious than we imagined in the days of classical physics". One may be "a pessimist as regards the possibility of understanding the inward nature of the world, but the scientist is an optimist, for his more modest goal is simply to find symbols to describe the world of experience and to test their power of predicting new experimental facts". "We climb one peak and make a short rest, but already the next and higher one awaits us."

Author and translator are both to be warmly congratulated on the production of a book which not only will appeal to a very wide public but will, on account of its clarity of exposition, be enjoyed by all who read it.

In one paragraph the adjective "western" is used to qualify the noun "science". L'art n'a pas de pays! Nicht wahr? J. H. B.

Soviet Science, by J. G. Crowther. Pp. x + 342. (Kegan Paul, Trench, Trubner and Co., Ltd.) 12*s*. 6*d*. net.

This excellent book is well worth reading. It is based on first-hand knowledge of the work which is being carried out in the various institutes described. The author is a frequent visitor to the U.S.S.R., and has acquired a thorough knowledge of the way in which the reconstruction of society in that country has affected the scientific work which is being carried out there; moreover he possesses accurate information concerning recent developments in science. The opening chapter on dialectical materialism is intended to form a background for the proper understanding of the developments described in the remainder of the book. In this chapter and in many other parts of the book will be found statements which will repay the most careful thought of those responsible for the organization of science in this country and its relation to our own society. For example, the various groups of research workers are responsible for the economics of their work and have to keep a record of all the expenditure incurred, a practice that might be followed with advantage in many institutions in this country. An interesting chapter on conferences contains some useful suggestions. The care of the various workers is described, and such facts as that "persons who work with X rays receive an addition to their annual holidays and are entitled to an extra daily milk ration free of charge" are worthy of note. The author makes some pointed remarks on the throttling effect of patent monopolies in the western countries. In one laboratory controlled by the war department the "visitor is followed at a distance of two paces, even through wind tunnels, by a pair of armed guards". In the chapter on biology we read the curious statement that "from the belief that physics is the more fundamental science, many Western European writers conclude that God is a physicist or a mathematician". Some parts of the book are rather in the nature of a catalogue and the lists of researches being carried out might have been more conveniently placed as appendices.

The book is well printed and contains 16 plates and an index. We have only noticed two or three minor misprints which no doubt will be corrected in future editions.

Whether the reader is interested in the relation of science to the structure of society or in the development of science itself, or even in the organization of some technical institute, he will find something in this book which will not only interest him but will also be of value to him in his work.

H. R. L.

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